Supercooled water survives in no-man's-land

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Citation: Physics Today **70**, 2, 18 (2017); doi: 10.1063/PT.3.3452
View online: http://dx.doi.org/10.1063/PT.3.3452
View Table of Contents: http://physicstoday.scitation.org/toc/pto/70/2
Published by the American Institute of Physics

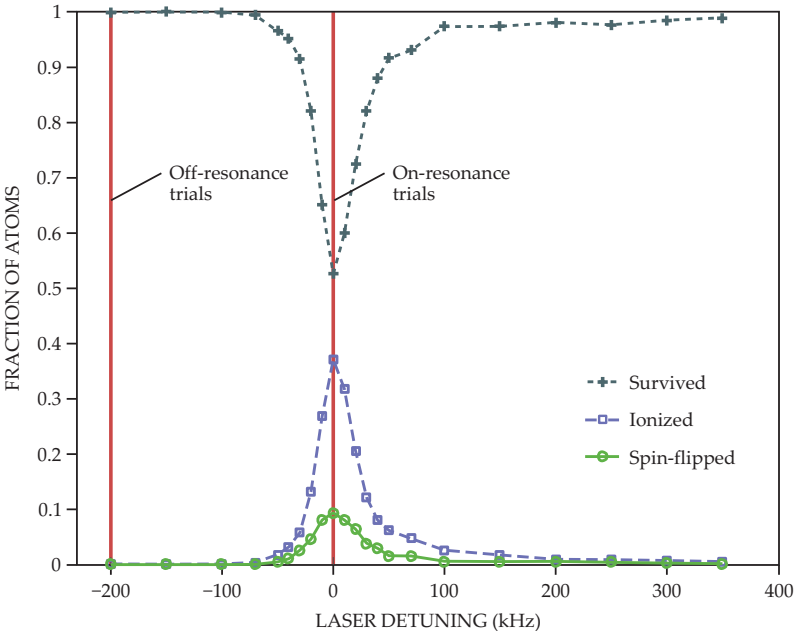

FIGURE 2. SIMULATED RESULTS of an antihydrogen spectroscopic experiment. Atoms that are excited by the laser may be ionized or spin-flipped and thus lost from the trap. So far, the ALPHA experiment has tested two values of the laser detuning, as marked by the red lines. The results for atoms remaining in and escaping from the trap are consistent with the simulation. (Adapted from ref. 1.)

Still, it's possible to make some educated guesses about what a matter–antimatter difference might look like. Because the revamping of quantum mechanics and general relativity could lead to unification of the two theories, one might expect the telltale spectroscopic difference to be on the natural size scale for unification effects: the ratio of the energy of electroweak processes to the Planck energy, or somewhere between 10^{-17} and 10^{-23}.

It's conceivable that spectroscopic measurements could eventually chip away at that range. But that would require progress not just in antihydrogen spectroscopy but also in hydrogen spectroscopy. The latter's precision is currently around 10^{-15}.

The ALPHA experiment resumes in May, and the researchers have a lot on their agenda. They want to get a detailed measurement of the 1*s*–2*s* transition by checking many more values of the laser detuning. They plan to explore the single-proton transition 1*s*–2*p*, which would open the door to laser cooling of antihydrogen. And they're building a new machine to study a different open question: In the gravitational field of a planet made of matter, do antimatter atoms fall up or down?

Johanna Miller

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Supercooled water survives in no-man's-land

A "stop-motion" crystallization experiment laid bare the liquid's behavior in a temperature range that was once considered inaccessible.

Water doesn't necessarily freeze at its freezing point. A skillful experimenter who maintains the liquid free of impurities can chill it well below 0 °C, or 273 K, in a metastable, supercooled state. In the 1970s chemists Austen Angell and Robin Speedy, then both at Purdue University, set out to determine just how cool water could go.[1] What they observed remains one of the biggest mysteries in thermodynamics: As their sample dipped below 250 K, its isothermal compressibility and heat capacity began to soar, indications that its density and entropy were fluctuating wildly at the molecular scale. Water seemed on the verge of some never-before-seen transformation. But before the drama could play out, the sample froze.

Unable to usher the liquid below 247 K, the researchers did the next best thing: They extrapolated their data. And they concluded that whatever the mystery transformation was, it happened at 228 K, where their power-law fits predicted a singularity.

In the decades since, several possible explanations have emerged—that the fluctuations were merely precursors to crystallization, for instance, or that they signaled the existence of a theretofore unknown liquid–liquid phase transition. (See the article by Pablo Debenedetti and Gene Stanley, PHYSICS TODAY, June 2003, page 40.) Speedy himself conjectured that 228 K marked the temperature at which water reached a thermodynamic bound known as a spinodal, beyond which a metastable liquid phase does not exist.[2]

A correct explanation, if one can be found, would do more than settle a decades-old debate. It would deepen scientists' understanding of other unusual properties of water, including the anticorrelation of entropy and volume observed at temperatures below 277 K. But the theories have proven all but impossible to scrutinize in the lab. That's because at 232 K, the so-called homogeneous nucleation temperature T_H, even pristine water will freeze—and freeze quickly. Just below that temperature, a crystalline phase spontaneously emerges in just tens of microseconds, even if no impurities are present to seed its growth.

Greg Kimmel and Bruce Kay, who have been experimenting with water for nearly two decades at Pacific Northwest National Laboratory (PNNL), knew there was little—no, nothing—they could do to slow down water's crystallization below T_H. So instead they devised a com-

bination of techniques that allowed them to speed up their observation times. In a newly published paper, they and their PNNL colleagues report the fruits of that labor:[3] the deepest experimental sortie yet into the no-man's-land of water's phase diagram below T_H. The results don't settle the mystery of water's fate in the supercooled regime, but they cull the contending theories.

Stop-motion crystallization

Chilling ordinary water is one way to create a supercooled liquid; melting ice is another. When liquid water is rapidly cooled to 136 K or colder at atmospheric pressure, it adopts a glassy form known as amorphous ice. In essence, its molecules freeze in place but maintain their liquid-like configuration. If the amorphous ice is then reheated past 136 K, the molecules jiggle free, and the water again behaves like a liquid.

For decades, researchers have been exploiting that roundabout path to the supercooled regime in order to experiment with water below T_H. At those extremely low temperatures, molecules diffuse sluggishly, so even though the thermodynamic driving force for crystallization is high, the kinetics are slow, and there's ample time to perform measurements. As the melted amorphous ice warms, however, the kinetics speed up. At the so-called crystallization-onset temperature T_x—roughly 160 K at atmospheric pressure—an experimenter ends up in a familiar bind: The melt crystallizes almost instantaneously. The region between T_x and T_H therefore constitutes a sort of no-man's-land; absent confirmation of a continuous thermodynamic path across it, one can't be sure the melt is truly a liquid phase, much less one that could illuminate the strange happenings near 228 K.

The PNNL researchers accessed that no-man's-land by using a pulsed IR laser to melt amorphous ice for nanoseconds at a time. As illustrated in figure 1, they deposited a 25-monolayer amorphous-ice film atop a crystalline-ice film, which coated a platinum substrate held at 90 K. When irradiated by an IR pulse, the amorphous layer thaws, warms above T_x, and begins to crystallize at the amorphous–crystalline interface. (Because the temperature never exceeds water's melting point, 273 K, the underlying crystalline film remains frozen.) Then, just as crystallization in the amorphous layer is getting under way, the heat dissipates, crystallization halts, and the remaining amorphous melt cools

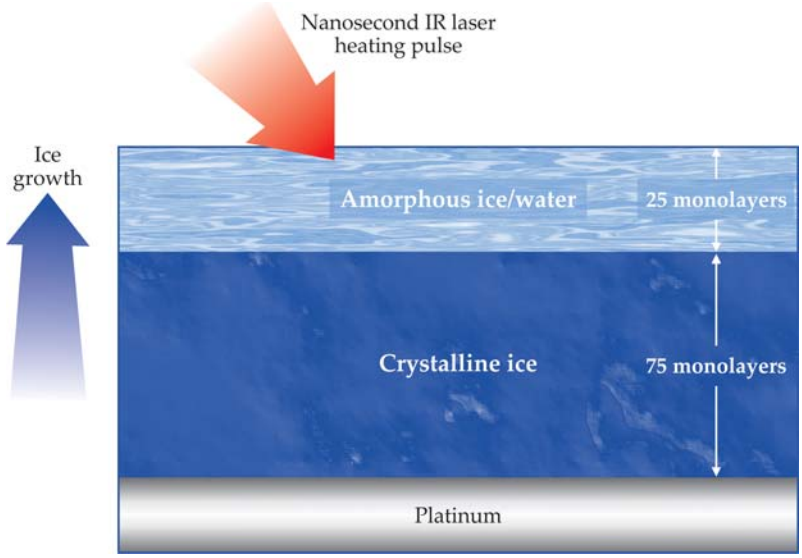

FIGURE 1. STOP-MOTION CRYSTALLIZATION. Researchers at Pacific Northwest National Laboratory observed the rapid crystallization of supercooled water using the 100-monolayer structure illustrated here. A 10 ns IR pulse melts the overlying amorphous-ice layer just long enough for it to partially crystallize at the interface with the underlying crystalline ice; the rest of the layer cools back to the amorphous-ice state. By repeating the pulses and monitoring the growth of new ice, the researchers could tease out crystallization rates and, by extension, dynamic properties of the liquid phase. (Adapted from ref. 3.)

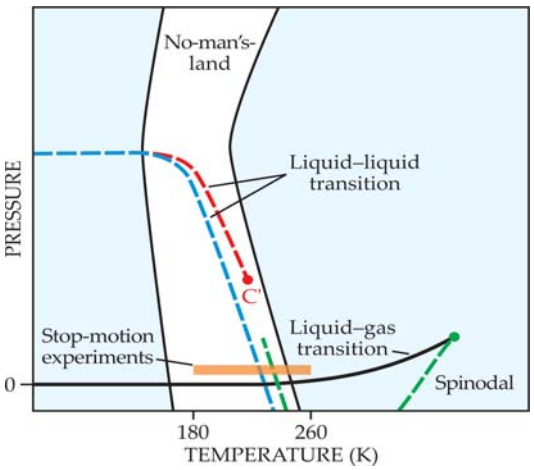

FIGURE 2. SEVERAL PHASE-DIAGRAM FEATURES have been hypothesized to explain supercooled water's behavior in an experimentally challenging "no-man's-land," including a liquid–liquid transition curve that terminates at a high-pressure critical point C′ (red); a liquid–liquid transition curve that dips to negative pressures (blue); and a spinodal (green) that decreases, then rises, in pressure as temperature falls. New "stop-motion" experiments exploring no-man's-land at vacuum pressures (orange bar) find no evidence of a spinodal or a liquid–liquid transition, but they don't rule out the possibility of a liquid–liquid transition with a high-pressure critical point.

back to the amorphous ice state. With each new pulse, the process repeats, and the amorphous–crystalline interface edges upward.

Kimmel likens the procedure to the stop-motion techniques Claymation directors used to make *Wallace and Gromit* and other films. "They make their clay figurines and then they take a picture. Then they move them a little bit and take another picture, and so forth. Then they make a movie out of it." Kimmel and his coworkers perform a similar trick with water, except instead of taking pictures, they use absorption spectroscopy to determine how much new crystalline ice forms after each thawing pulse. From that growth rate, the researchers can infer the liquid's diffusivity, which serves as a window into its thermodynamics.

In 2014 a collaboration led by Anders Nilsson of SLAC used femtosecond x-ray pulses to investigate water microdroplets cooled into no-man's-land,[4] but only to temperatures near 228 K—not quite low enough to rule conclusively on Speedy's spinodal conjecture or competing theories. The PNNL team, by contrast, was able to measure diffusivities between 180 K and 260 K, nearly the full width of the elusive region.

The limiting factor below 180 K was the PNNL researchers' own patience. The number of IR pulses required to crystallize the film of amorphous ice grew sharply as the measurement temperature fell, explains Kay. "We could explore something like a million pulses in a 24-hour period. It took our postdoc Yuntao Xu three days to get the lowest data point." Once the team had measurements down to 180 K, however, a smooth interpolation could be drawn to connect the diffusivity curve with one obtained by conventional means below 160 K.

A tale of two liquids?

The PNNL team found that water's diffusivity declines steeply but continuously as its temperature falls through no-man's-land. Even as the data pass through Speedy's hypothesized spinodal (the green curve in figure 2) there's no hint of a kink that would signal a thermodynamic singularity.

To David Limmer, a chemist at the University of California, Berkeley, the smoothness of the curve definitively rules out the spinodal conjecture—especially in light of Nilsson and company's results, which hinted at a similar conclusion. "The fact that you can have a smooth continuation of the high-temperature diffusion data to the lower-temperature data is certainly suggestive of a well-defined metastable liquid at temperatures lower than many people had expected."

But could there be two well-defined liquids? A popular explanation of the fluctuations in the Angell–Speedy experiment is that they stem from the existence of a first-order transition between a high-density liquid phase and a low-density one exhibiting a more ice-like molecular configuration. That theory would also neatly explain the sharp density jumps seen when amorphous ice is cycled above and below pressures of about 2 kbar. (See PHYSICS TODAY, December 2013, page 16.) But the PNNL experiments produced no hints of such a transition.

Even to many proponents of two-

liquid theories, that isn't terribly surprising. To precisely control the thickness and structure of their water films, the PNNL researchers performed their experiments under vacuum. Although some two-liquid theories predict a first-order phase transition at vacuum pressures (see the blue curve in figure 2), most predict that the liquid–liquid equilibrium curve extends down only to a critical point located at several hundred times atmospheric pressure (red curve). To test those scenarios, the PNNL group would have to adapt its technique for high-pressure operation, a task that Kay says "would be tricky, but possibly doable."

For now, the researchers have set their eyes on a different experimental prize: measuring the homogeneous nucleation rate of water throughout no-man's-land—data that would provide a coveted benchmark for numerical models.

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Semiconductor metamaterial fools the Hall effect

A structure made entirely out of an n-type semiconductor can mimic some properties of a p-type semiconductor.

Much to the confusion of many beginning physics students, electric current vectors are conventionally written as if they represented the flow of positive charge: The direction of the current is opposite to the direction in which electrons actually move. The convention has its origins in Benjamin Franklin's one-fluid theory of electricity. Lacking evidence to the contrary, Franklin assumed that the phenomena he observed resulted from the movement of a positive "electric fire." The theory was mostly serviceable: There's often little to distinguish a positive charge moving in one direction from a negative charge moving in the other.

One way to tell the difference is via the Hall effect, the appearance of a transverse voltage when an electric current passes through a magnetic field. Charge carriers are deflected in the direction that corresponds to the cross product of the (conventionally written) current and the field. If the charge carriers are positive, they produce a voltage gradient in the same direction. If they're negative, the gradient is in the opposite direction.

The Hall effect provides experimental evidence that currents in metals arise from the flow of negative charge. It also offers a way to distinguish between n-type semiconductors, whose charge carriers are also electrons, and p-type semiconductors, whose charge carriers are positively charged holes.

But the relationship between charge-carrier sign and Hall voltage is not always so simple, as Martin Wegener and his colleagues at the Karlsruhe Institute of Technology in Germany have now experimentally shown.[1] Using an n-type semiconductor, the researchers crafted a microstructured metamaterial, shown in figure 1, that behaves like a p-type semiconductor—at least as far as the Hall effect is concerned.

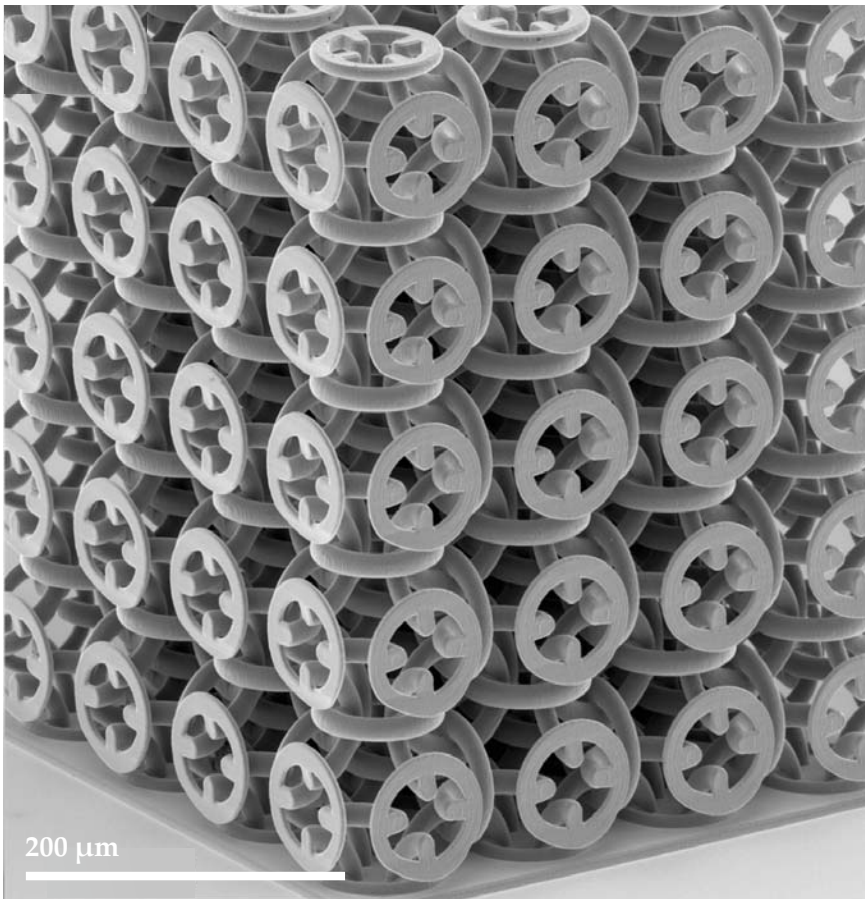

FIGURE 1. INSPIRED BY MEDIEVAL ARMOR. The metamaterial shown in this electron micrograph is a periodic array of linked hollow rings. Made of n-type zinc oxide, it exhibits the Hall signature of a p-type material. (Adapted from ref. 1.)

Science mirrors art

The literature is full of examples of metamaterials with electromagnetic, acoustic, or mechanical properties that are qualitatively different from those of their constituents. For example, metamaterials can be designed to have both negative electric permittivity and negative magnetic permeability (or, more simply, a negative index of refraction), despite the fact that there are no such bulk materials in nature.