

eight more years at Weizmann, he went to Stanford in 1987.

Arieh Warshel was born in November 1940 in kibbutz Sde Nahum in what is now Israel. Working in Lifson's group, he earned his PhD from Weizmann in 1969. After two years as a post-doc in Karplus's group, he returned to Weizmann to join the faculty. He has been at the University of Southern California since 1976.

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"Melting" ice yields hints of a second liquid water phase

New experimental findings bolster a controversial theory of supercooled water.

Water can be peculiar at times. At temperatures near freezing, it expands as it's cooled. It can become less viscous as it's compressed. And, according to a theory proposed two decades ago by researchers at Boston University, it can exhibit yet another striking behavior: It can form two liquid phases.¹ (See the article by Pablo Debenedetti and Gene Stanley, *PHYSICS TODAY*, June 2003, page 40.)

The two-liquid hypothesis was inspired by molecular-dynamics simulations that showed supercooled water forming low- and high-density liquids (LDL and HDL) at temperatures below about 220 K. In LDL, water appears to form a hydrogen-bond network similar to that of common ice, with each molecule sitting inside a tetrahedral cage formed by its four nearest neighbors. In HDL, up to two extra molecules squeeze into the interstices of each tetrahedral cage.

The hypothesis has its detractors. David Chandler (University of California, Berkeley) and coworkers, for instance, argue that only one of the liquids can be a true phase corresponding to a metastable equilibrium; the other is likely a nonequilibrium transient state that forms as water freezes to crystalline ice.² That view is backed by numerical work suggesting that HDL and LDL don't form stable interfaces, which are hallmarks of a two-phase system.³

Now a collaboration led by Thomas Loerting (University of Innsbruck, Austria) and Roland Böhmer (Technical University of Dortmund, Germany) has weighed in on the matter with new experimental evidence.⁴ The researchers used a pair of independent techniques

to probe water's phase changes in the deeply supercooled regime. Although their findings don't close the book on the water controversy, they strengthen the case for two liquids.

A pair of glasses

The plausibility of the two-liquid theory stems in part from the well-known existence of two amorphous ices: low- and high-density amorphous ice (LDA and HDA), shown in figure 1. LDA can be made by rapidly cooling water droplets to liquid-nitrogen temperatures. HDA is typically made by chilling crystalline ice to liquid nitrogen temperatures and then compressing it to around 10 kbar.

So-called glassy states, amorphous ices have the mechanical properties of a solid but the disordered molecular configurations of a liquid. When heated above their respective glass-transition temperatures, they melt—or, more precisely, relax—to form ultraviscous supercooled liquids that, though metastable, can persist for hours. With respective densities of about 0.92 g/cm³ and 1.15 g/cm³, those liquids are thought by many to be the LDL and HDL posited by the two-liquid theory.

But are the liquids distinct phases? One way to test is to probe their phase-transition behavior. In a pure substance, a phase transition such as the glass transition has a single thermodynamic degree of freedom; fixing the pressure fixes the transition temperature. (Technically, the glass transition is a kinetic, not an equilibrium, transition, so its temperature at a fixed pressure may vary by a few K depending on the sample preparation.) If LDA and HDA



Figure 1. Amorphous ice can exist in high-density (**top**) and low-density (**bottom**) states, depending on the pressure at which it forms. The two samples shown here, inside 7-mm-diameter rings, have identical mass. (Images courtesy of Osamu Mishima.)

were to exhibit vastly different glass-transition temperatures at a single pressure, it would serve as a clue that the ices—and the low- and high-density liquids they form when they relax—are also distinct.

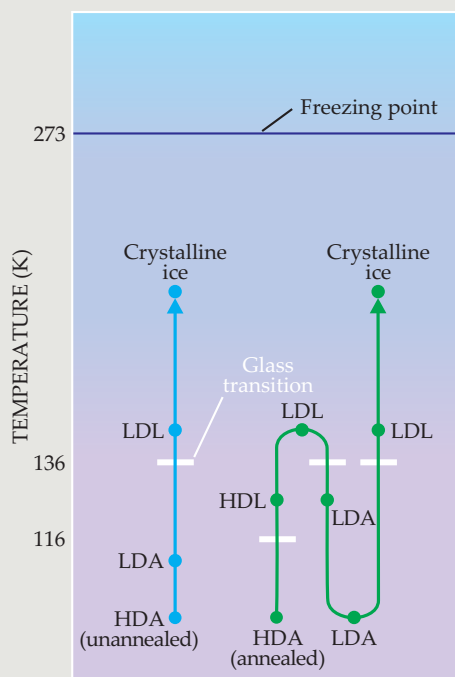
Hot and cold

Observing both glass transitions at common pressure turns out to be technically complicated. HDA is fairly unstable at low pressures, and LDA is unstable at high pressures. So although LDA's glass transition is straightforward to detect at say, ambient pressure, HDA under the same conditions tends to transform to LDA before becoming warm enough to relax.

One way to improve a glass's stability is to anneal it—to maintain it for an

Figure 2. Water's transformations.

When heated, unannealed high-density amorphous ice (HDA) undergoes the phase-transition sequence shown at left: HDA converts to low-density amorphous ice (LDA) at roughly 110 K; LDA undergoes a glass transition (white bar) to low-density liquid (LDL) at 136 K; and at higher temperatures LDL forms crystalline ice. By contrast, annealed HDA remains stable up to 116 K, where it undergoes a glass transition to high-density liquid (HDL). Applying the heating and cooling protocol shown at right, it's possible to detect both glass transitions in a single experimental run.



extended time at the brink of its glass transition and thereby allow it to adopt a more energetically favorable, but still disordered, molecular configuration. Five years ago, Loerting's grad student Katrin Amann-Winkel began developing annealing protocols for HDA. She found that annealing yielded HDA samples that remained stable to significantly higher temperatures—possibly high enough to detect an ambient-pressure glass transition.

Loerting, Amann-Winkel, and their

collaborators set out to find that transition using a pair of experimental techniques. The Innsbruck group performed a calorimetry experiment, in which one tracks how a sample's heat capacity varies with heating and cooling. Sudden rises in heat capacity indicate endothermic events like relaxation and melting; sharp falls indicate exothermic events such as freezing. The Dortmund group, meanwhile, studied identically prepared samples using dielectric spectroscopy. In that method,

liquefaction is detectable as a telltale decrease in a sample's dielectric relaxation times.

As sketched at left in figure 2, an ambient-pressure heating run performed on unannealed HDA reveals just one glass transition: HDA converts to LDA at around 110 K; LDA undergoes a glass transition, to LDL, at 136 K; and LDL eventually freezes to crystalline ice.

By contrast, the experiments with annealed HDA, depicted at right in the figure, reveal a second glass transition, from HDA to HDL, at 116 K. At higher temperatures, HDL expands to the more stable low-density form, LDL. Recooling and reheating the LDL reveals the more familiar glass transition at 136 K as LDL converts to LDA and back.

The existence of two glass transitions is a hint of two liquids but not a proof. More definitive would be to show that the two liquids can coexist and transition reversibly between one another. Such studies may not be far off. Both liquids are robust, says Loerting. "We can maintain them for hours without any signs of transformation, provided we work at the right temperature. That should allow us to do a lot of experiments."

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physics update

These items, with supplementary material, first appeared at <http://www.physicstoday.org>.

Fiat LUX: Dark-matter detector's initial results. The nature of the dark matter that makes up some 85% of the material stuff of the universe remains a mystery. Current consensus favors a weakly interacting massive particle, or WIMP, inspired by extensions of the standard model of particle physics. One approach to understanding those putative particles is to look for their rare interactions with conventional matter. A number of experiments have undertaken such searches. Last week the most sensitive of them, the LUX (Large Underground Xenon) experiment, announced via webcast its first results. The experiment's initial three-month run saw no evidence of WIMPs, which significantly lowered the upper limits for the mass-dependent WIMP interaction strength. Moreover, the new results ruled out the handful of possible light-WIMP sightings that had been reported earlier. Located 1.5 km belowground at the Sanford Underground Research Facility in Lead, South Dakota, the LUX detector monitors 250 kg of liquid xenon. When a WIMP collides with



the cosmic-ray problem; a surrounding tank filled with pure water provides additional shielding. The LUX researchers plan to collect data for another two years. The collaboration's next-generation detector, already being planned, will contain 20 times the xenon of LUX and will be so sensitive that it will see background neutrinos. (D. S. Akerib et al., LUX collaboration, <http://arxiv.org/abs/1310.8214>.)

—SKB