Fast vs slow water—explaining the fragile-to-strong transition

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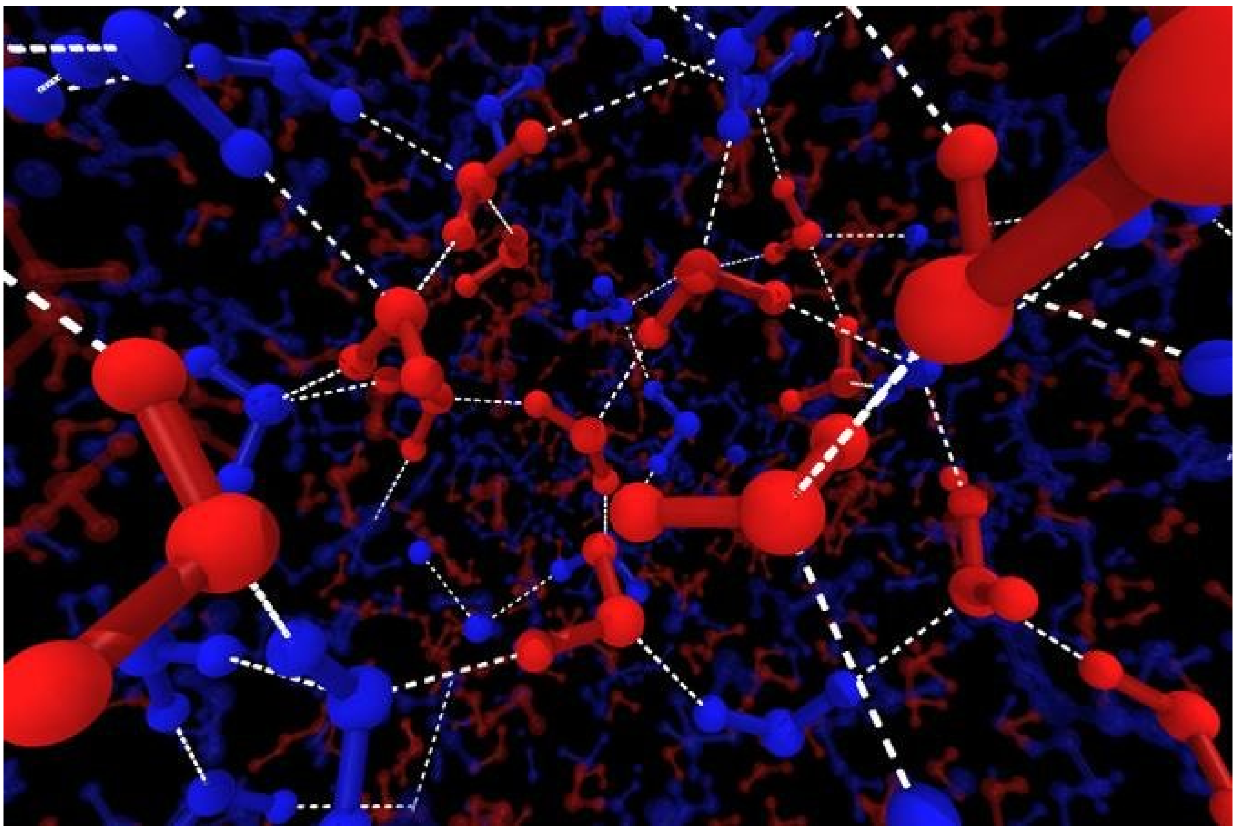

Illustration of water's local structures. The blue lines show the H2O molecules of tetrahedral structure, the red lines show H2O molecules of disordered structure. The large balls show oxygen atoms, the small balls show hydrogen and the dotted white lines represent Hydrogen bonds. Credit: 2018 Hajime Tanaka, Institute of Industrial Science, The University of Tokyo

A Japanese research team led by The University of Tokyo investigated the fragile-to-strong transition of water. Unlike most liquids, when water is cooled, the rate of increase of its viscosity reaches a maximum at a certain low temperature. The team showed that modeling water as a temperature-dependent mixture of two states—disordered fast water and locally ordered slow water—explained the fragile-to-strong transition and avoided the faulty predictions of earlier theories based on glassy behavior.

Water is strange in many ways. Some of its chemical quirks are familiar, such as expanding when it freezes to ice. A lesser-known curiosity, which it shares with just a few other liquids, is the fragile-to-strong transition. Explaining this behavior, which relates to how cold water flows, has long been a source of debate. Now, a convincing explanation has been put forward by researchers in Tokyo.

When liquids cool, their dynamics slow down and they become viscous. For most liquids, the rate of slowing is constant as a function of temperature and these are known as strong liquids. For fragile liquids, however, the rate continually increases as the temperature drops. Water is unusual in this regard—it is fragile at room temperature, but strong at low temperatures, where its rate of increasing viscosity hits a peak.

This fragile-to-strong transition is elusive, occurring only in the supercooled regime, below water's usual freezing point. Early models tried to link it to glassy dynamics, as supercooled water is known to be a glass-former. However, a team led by The University of Tokyo's Institute of Industrial Science (IIS) proposes a two-state theory, in effect modeling water as a mix of two co-existing liquids.

Mathematically, the strong/fragile distinction rests on the Arrhenius law for dynamical processes—strong liquids obey this law, but for fragile ones, the rapid increase of viscosity is super-Arrhenius. As reported in the journal *PNAS*, the IIS team amended this view by considering water to consist of two states, termed "fast" and "slow," which are structurally different, but both obey Arrhenius dynamics.

"We simulated water by molecular dynamics and looked for structural patterns," explains study co-author Rui Shi. "H2O molecules always assemble into tetrahedra, but we saw that some of these local structures were highly ordered, others less so." The disordered states correspond to fast water, and dominate at high temperature, while the well-ordered slow state takes over as the sample cools.

Crucially, the equations derived from the two-state model successfully predict the fragile-to-strong crossover. This happens well above the glass transition point—glassy behavior seems to be a red herring as far as this issue is concerned. The fact that fast water has Arrhenius, rather than power-law, dynamics also resolves faulty predictions based on earlier attempts to link water's fragility to certain aspects of its phase diagram.

"Fragile water may be an illusion. The apparent transition is an artifact of the temperature-dependent balance of two strong liquid states," says lead author Hajime Tanaka. "The presence of two states reflects water's tendency to form local structures, which is easier at low temperature. In fact, other liquids with a fragile-to-strong transition, like silica, also show local ordering. We propose that this, rather than any glassy behavior, is what distinguishes them from true fragile liquids."

More information: Rui Shi el al., "Origin of the emergent fragile-to-strong transition in supercooled water," *PNAS* (2018). www.pnas.org/cgi/doi/10.1073/pnas.1807821115

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