

Researchers demystify glasses by studying crystals

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Glass is something we all know about. It's what we sip our drinks from, what we look out of to see what the weather is like before going outside and it is the backbone to our high speed communications infrastructure (optical fibers).

But what most people don't know is that "glass transitions," where changes in structure of a substance accompanying temperature change get "frozen in," can show up during cooling of most any material, <u>liquids</u> through metals. This produces "glassy states," of that material – exotic states that can be unfrozen and refrozen by merely changing the temperature a little up and down around the transition temperature.

"For liquids," says C. Austen Angell, an Arizona State University Regents professor of chemistry and biochemistry and a leading explorer in this domain, "it's fairly simple, glasses form when crystals don't." Beyond this "banality," as Angell calls it, things get more complicated.

Angell has done considerable work in this realm, the best known of which has been on the classification of glass-forming liquids between extreme types – "strong" liquids, like the silica glass that optical fibers are made from, and "fragile" liquids which glassblowers stay away from because, during cooling, they set up solid too quickly for them to work with.

Now another piece of the puzzle is being reported on what, exactly, glasses are. The report uses the unusual behavior of a non-liquid



substance to help unlock the secrets. It is a metallic alloy consisting of equal parts of cobalt and iron.

In a paper in the Nov. 28, 2010, issue of *Nature Physics*, Angell and his colleagues – Shuai Wei, Isabella Gallino and Ralf Busch, all of Saarland University, Germany – describe the behavior of iron-cobalt ($Fe_{50}Co_{50}$) superlattice material as it cools down from its randomly ordered high temperature state. The paper, "Glass transition with decreasing correlation length during cooling of Fe50Co50 superlattice and strong liquids," builds on work from 1943 by Kaya and Sato in Japan who measured the heat capacity of the bi-metallic alloy.

Heat capacity is the amount of energy it takes to heat a sample by one degree Kelvin. Albert Einstein thought heat capacity was a material's most revealing property.

The iron-cobalt alloy heat capacity showed two features – a sharp spike at 1000 K (1340 F) called a lambda transition (which is quite common in <u>metal</u> alloys as the two types of atoms order themselves onto two individual interpenetrating lattices) – and near 750K (890 F) another feature which is very unusual for a metallic crystal, a glass-like transition, where the state of order gets "frozen in" during cooling.

Most glassy forms of matter experience a gradual increase in heat capacity as they are heated until this special transition point is reached. At this point (called the glass temperature) the materials suddenly jump to a new, higher heat capacity zone, often 100 percent higher, and change from a solid material to a very viscous liquid.

What the new measurements in the *Nature Physics* article show is that the disordering of the superlattice has the kinetic characteristic of strong liquids. But because the alloy lambda transition is well understood, researchers know that a property called the "correlation length" is



decreasing as the temperature decreases from the lambda spike towards the (glass) transition temperature. This is the opposite behavior from what has been thought to be characteristic of liquids as they cool towards their transition temperature.

"We now argue that strong and fragile extremes are not really extremes, so much as they are opposites," Angell said.

"On a molecular level, we now think that in the strong liquids the organization of molecules in space is getting shorter-range as the glassy state is approached, while in the fragile liquids, that organization length is indeed getting longer as people have already proposed," he explained. "This shows that static correlation length changes do not, by themselves, account for the liquid turning solid at the glass transition."

To understand the paradox Angell turned to the substance water. Water is famous for having strikingly anomalous properties in its super cooled state. As 228 K (-49 F) is approached, water's <u>heat capacity</u> is racing up like that of iron-cobalt alloy at its critical point. Scientists now believe that water would show the same sort of spike if it didn't crystallize first. When water is quenched at a million degrees per second it doesn't crystallize and a glass that acts like a low temperature replica of silica results, i.e. a strong liquid. Angell sees water's behavior as a sort of Rosetta stone.

"The Rosetta stone has two faces, the same statement on each but in a different language," he said. "In my case, water speaks the language of fragile liquids on its upper face (at temperatures more than 228 K, or -49 F), and the language of strong liquids on its lower face (temperatures less than 228 K)."

Previous work by Angell (with Robin Speedy in 1976) pinpointed the 228 K temperature as a "divergence temperature" of a special



mathematical law, called a power law, typical of critical systems, which described the physical properties of super cooled water.

"So now we see strong liquids and fragile liquids as occupying opposite flanks of some generalized 'order-disorder' transition," Angell explained. Angell and his colleague Dmitry Matyushov in ASU's physics department, plan to describe this generalized transition in more detail in the future.

Meantime there are practical benefits to be had. Angell points out that if <u>optical fiber</u> glasses, being silica or silica-like, have shorter range organization at lower temperatures, then fibers that have been annealed at lower temperatures than their fiber-drawing temperature (more than 2000 K) should be less scattering of light, hence better for communications purposes. Thus this new information can mean better performing materials in the future.

"Patent literature suggests that the fiber optics scientists already learned the benefits of annealing (a heat treatment that alters the microstructure of a material causing changes in properties such as strength, hardness and ductility). Now we would know exactly why this is so, and we could actually design that property into the material forming process," Angell said.

Provided by Arizona State University

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