Scientists confirms liquid-liquid phase transition in silicon

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Using rigorous computer calculations, researchers from Carnegie Mellon University and the Carnegie Institution of Washington have established evidence that supercooled silicon experiences a liquid-liquid phase transition, where at a certain temperature two different states of liquid silicon exist. The two states each have unique properties that could be used to develop new silicon-based materials. Furthermore, the methods developed can be applied to gain a better understanding of other materials.

The findings will be presented Friday, March 20 at the American Physical Society's March Meeting in Pittsburgh. The results also were published as an Editor's Selection in the Feb. 20 issue of Physical Review Letters.

Under normal conditions, phase transitions occur when the structure of a substance changes in response to a change in temperature and/or pressure. The most commonly thought of phase transitions are between solids, liquids and gases. However, it was recently discovered that some substances experience phase transitions within the same state, resulting in two different forms with their own individual characteristics. For example, it's thought that water has a liquid-liquid transition.

"Water and silicon share many unusual characteristics. For example, in most materials, their solid states are denser than their liquid states, but in water and silicon the opposite is true. That's why ice floats on water and solid silicon floats on liquid silicon," said Michael Widom, professor of

physics at Carnegie Mellon. "The unusual volume expansion of frozen water and silicon that causes them to float is probably connected to the existence of a liquid-liquid transition."

Like water, it has been hypothesized that supercooled silicon — liquid silicon that has its temperature lowered to below the freezing point without crystallizing and becoming a solid — experienced a liquid-liquid phase shift. Computer simulations initially predicted the existence of two liquid phases, but further simulations and experiments failed to produce the necessary evidence to prove their presence.

To resolve the disparity between the prior experiments, Carnegie Mellon's Widom and Carnegie Institute of Washington post-doc Panchapakesan Ganesh, who began this work as a graduate student in Widom's lab, used rigorous first-principles calculations based on quantum mechanics to, for the first time, prove the existence of a liquid-liquid transition in silicon. First-principle calculations start with established laws of physics, and make no assumptions or approximations, leaving little room for question. Such calculations provide the most accurate predictions for the structural properties at high pressures and temperature, since conducting actual experiments in these conditions is near impossible.

Since the calculations are based on quantum mechanics, they were extremely complex and time-consuming. It took one month of computing time to complete the calculations needed to determine the molecular dynamics of silicon at one single experimental temperature and volume. The researchers applied novel methods of parallel tempering and histogram data analysis to look at nine temperatures and 12 volumes. The calculations required nine CPU years to be completed, but the experiment took only one actual calendar year because the calculations ran in parallel on many computers.

The computations revealed that a liquid-to-liquid phase shift, evidenced by the presence of a van der Waals loop, occurred when silicon was supercooled to 1200 degrees Kelvin; silicon normally freezes at 1700 degrees Kelvin. A van der Waals loop occurs when pressure grows as volume increases, marking a thermodynamically unstable situation. The unstable condition is resolved by transforming into two coexisting states of differing densities — in this case two distinct forms of liquid silicon, each having its own unique and dissimilar properties. One was high density and highly coordinated with metallic properties, much like normal liquid silicon, and the other was low density, low-coordinated and semi-metallic, with a structure closer to that of solid silicon.

"This study shows that accurate calculations based on quantum mechanics can now answer long-standing questions about familiar and unfamiliar materials," Widom said.

The simulation methods used by the researchers are a breakthrough on their own. The computational methods can be applied to achieve a better understanding of a wide range of elements and molecules and how they behave at extremely high temperatures. Revealing the structure and properties of different elements and compounds at previously untestable conditions could lead to the development of new materials with commercial applications. Widom, for example, is now using the tools to study metallic glass, a solid metal with the structure of a liquid that contain desirable properties not found in commonly used alloys.

Source: Carnegie Mellon University