Forget the freezer: Research suggests novel way to control water behavior

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Researchers may be able to "freeze" water into a solid, not by cooling but by confining it to narrow spaces less than one-millionth of a millimeter wide, according to new results from an interdisciplinary team of scientists and engineers.

It's more than a neat trick -- a deeper understanding of how thin films of water behave in nanometer-sized spaces may help advance numerous scientific endeavors, including the development of new energy sources, pharmaceuticals and self-cleaning surfaces.

Water has long been known for its quirky physical properties, including its ability to expand when cooled and to flow with increasing ease when compressed. While this behavior on a large scale has been the subject of much research, the effect of nano-confinement on water's physical properties and transitions between the gas, liquid and solid phases is largely unknown.

"This research suggests the idea that phase transitions can be controlled by understanding the effects of confinement and interaction with a surface," said team member Pablo Debenedetti, vice dean of Princeton University's School of Engineering and Applied Science and the Class of 1950 Professor in Engineering and Applied Science.

In addition to Debenedetti, the research team includes Nicolas Giovambattista, a former Princeton postdoctoral research associate now a physicist at Brooklyn College of the City University of New York, and

Peter Rossky, a chemist at the University of Texas-Austin. The researchers published their findings Feb. 6 in the journal *Physical Review Letters*. Their work is part of an ongoing effort funded by the National Science Foundation to study how confinement in nanometer-scale spaces affects the behavior of water-based solutions, including those containing biomolecules.

In their investigation, the researchers used computers to simulate the movement of water molecules trapped between two hypothetical plates. The plates in the scenario were hydrophobic, or water-fearing, meaning they repel water much like the surface of a leaf.

When the distance between the two plates was narrowed to roughly the width of three water molecules, the simulations demonstrated a previously unknown phase of water consisting of a layer of mobile water sandwiched between two layers of "frozen" water adjacent to each plate. The layers were each one-molecule thick and, in the simulated environment, remained at room temperature.

The "ice sandwich" phase persisted throughout the length of the simulation, some two nanoseconds (two-billionths of a second) long. Though brief by most standards, this is a long period of time as simulations go, indicating that the phase would persist indefinitely without the middle layer freezing, if conditions were kept stable, said Debenedetti.

When the density of the system was reduced, the three-layer phase transitioned into two layers of fluid -- again, still at room temperature.

"Methodologically, it is a very nicely done piece of work, in which complex phase behavior is investigated systematically through the power of state-of-the-art computing," said H. Eugene Stanley, professor and director of the Center for Polymer Studies at Boston University.

"Phenomenologically, their findings are very striking. In particular, the observation that a tri-layered system, with two frozen layers sandwiching a fluid intermediate layer, can exist as an equilibrium state because of confinement is very exciting."

Debenedetti noted there are numerous applications for an increased understanding of the fundamental behavior of water under confinement. For example, hydrogen fuel cells, which are thought to be promising for use in vehicles and stationary power production, generate electricity by passing hydrogen ions across a membrane where water is confined in nano-scale channels.

"This is the perfect example of confined water, where a molecular-level understanding will have considerable practical applications," Debenedetti said.

The work may also advance the ability to understand how different surfaces can be used to affect the behavior of water alone and mixed with other substances. This knowledge could one day inform the development of innovative separation techniques for use in the production of biofuels. One problem with these fuels, such as ethanol, is that they contain water when first obtained from the plants. Being able to design surfaces that interact with water and ethanol differently might provide a new method to remove the water.

"Since much of biology involves water under confinement, perhaps the greatest utility of this work will be in a better understanding of biological processes," said Salvatore Torquato, professor of chemistry and the Princeton Institute for the Science and Technology of Materials. "This potentially has applications in drug discovery, for example."

While the potential applications are intriguing, Debenedetti cautioned that even the best simulations cannot be taken as exact representations of reality. They do, however, often provide insights into molecular behavior and suggest new research avenues to pursue.

As next steps, the researchers intend to explore how changing the conditions in the simulation alters the behavior of water. This includes using hypothetical walls that are not perfectly smooth, varying the temperature, and using theoretical water that contains dissolved solutes, such as salt.

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