New finding bubbles to surface, challenging old view

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Chemical engineers have discovered a fundamental flaw in the conventional view of how liquids form bubbles that grow and turn into vapors, which takes place in everything from industrial processes to fizzing champagne.

The findings cast into doubt some aspects of a theory dating back to the 1920s that attempts to describe the underlying molecular mechanism behind a phenomenon called "homogeneous nucleation," said David S. Corti, an associate professor of chemical engineering at Purdue University.

The research could lead to a more precise understanding of the "phase transition" that takes place when bubbles form, grow and then become a vapor, which could, in turn, have implications for industry and research, Corti said.

In the conventional view, a liquid boiling and turning into a vapor takes place in a systematic process known as "nucleation and growth." The liquid first forms tiny "nuclei," or microscopic bubbles, that eventually grow as they pick up particles like a snowball gaining size as it rolls down a hillside. This conventional view is described by "classical nucleation theory," which was originally proposed in the 1920s.

"Our findings indicate that this is not what's going on," Corti said. "The bubble grows via a mechanism very different from classical nucleation theory."

Findings are detailed in a research paper appearing online this month in the journal *Physical Review Letters*. The paper was written by Corti and chemical engineering doctoral student Mark Uline.

As water is heated in a pot on a stovetop, it begins boiling when the temperature reaches 100 degrees Celsius, or 212 degrees Fahrenheit.

"You get little microscopic bubbles that form on the surfaces of the pot," Corti said.

This bubble formation on a surface is called heterogeneous nucleation. Bubbles also may form, however, by homogeneous nucleation, in which they appear not on surfaces, but within the liquid itself. The new findings specifically apply to homogeneous nucleation.

"A common example is when you heat water in a microwave oven," Corti said. "It heats liquid from the inside as opposed to on the surface, so you can actually raise the temperature of the water above 100 degrees Celsius and it doesn't boil. Sometimes when you microwave water in a mug you can superheat it and, if you put a spoon in there after removing it from the microwave, you introduce nucleation sites and it boils off and sprays hot water. The transition happens rapidly, causing a vapor explosion."

The conventional nucleation theory uses the same mechanism for how liquid droplets condense from a vapor in attempts to describe how bubbles form in a liquid. The Purdue researchers found, however, that bubbles do not form by the same mechanism as condensing droplets, Corti said.

According to the conventional theory, the pathway going from a liquid to a vapor is narrow, strictly defining the molecular mechanism by which the liquid becomes a vapor.

"You could think of this pathway as a mountain pass," Corti said. "In order to get from the liquid to the vapor, you have to go over this mountain pass. If you climb up and you're not quite at the top, sometimes you can roll back down, but if you get to the top, you can roll down to the other side and get to the vapor phase."

The new research has shown that this metaphorical mountain pass is actually more broad and flat than previously thought, meaning there are several possible pathways responsible for the phase transition.

"At the same time, what we found is that once you get over this mountain pass, which is called the free energy surface of bubble formation, the surface disappears," Corti said. "You look at one side and you see the mountain and think everything is OK, but once you climb over, it's as if the mountain disappears on the other side."

In the conventional view, the forming bubbles moving down the mountain pass could, in principle, reverse direction back toward the liquid phase.

"But in our view, as soon as you get over the top of the mountain, the mountain disappears," Corti said. "You have no choice but to plummet to something else, the vapor phase."

The findings were based on research using new theoretical methods and verified by computational simulations developed by the Purdue engineers.

Nucleation occurs when a liquid is heated above its boiling temperature or when the pressure exerted on a liquid is decreased below the so-called saturation pressure, which is the case when the lid is removed from the bottle of a carbonated beverage such as champagne, beer or a soft drink.

"This also occurs in the chemical industry and in other work environments where liquids flow through pipes, sometimes with undesirable consequences," Corti said. "Depending on the diameter of the pipes, the pressure of the liquid can drop very rapidly, causing it to become superheated, and before the pressure recovers you can get this phase transition."

The bubbles that form can then collapse when the pressure increases again, sometimes causing significant damage to equipment.

In other industrial processes involving propeller blades, bubbles can form or undergo "cavitation" and then suddenly implode, producing high temperatures and extreme pressures and damaging equipment.

"There are tons of examples, but the real fundamental mechanism underlying what's going on is not that well understood, even for very simple systems," Corti said.

New insights into phase transition could translate into practical and safety benefits for industry. Such insights also could result in a better understanding of the mechanisms responsible for initiating "sonochemistry" and "sonoluminescence" processes in which sound waves are used to form tiny bubbles in liquids. As the bubbles collapse, they emit flashes of light and generate high pressures and temperatures that could be used to enhance chemical reactions.

Another potential practical benefit is to improve the manufacture of foams made of plastic polymers that depends on the formation and distribution of bubbles.

Although the new findings indicate current theory does not adequately describe the molecular mechanism for bubble formation and phase transition from a liquid to vapor, the Purdue researchers do not yet know precisely what that mechanism is.

"We are still working out the full implications of this ourselves," Corti said.

Source: Purdue University

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