SCIENCE NEWS

THE WEEKLY NEWSMAGAZINE OF SCIENCE

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puzzling mathematics

homocysteine's fracture factor

undersea asphalt found

youngest galaxies observed?

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not a bubble

ANTIBUBBLES GET A CLOSE LOOK

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Cover What looks like a bubble but isn't one? An antibubble. Noticed occasionally since the 1930s, this surprising underwater structure—a water droplet inside a shell of air submersed in water—is only now receiving serious study. Scientists are exploring how it forms, how it pops, and how it might produce unusual foams. (T. Fritz) Page 311

THE RISE OF ANTIBUBBLES

Odd, soggy bubbles finally get some respect

BY PETER WEISS

Two years into his doctoral research, which had him looking long and hard at bubbles rising in a liquid, Alberto Tufaile noticed something odd. Sometimes, a few small bubbles would circle around in his flasks instead of rising to the top. "I was worried because I couldn't explain what I was seeing," recalls Tufaile, now a physicist at the University of São Paulo in Brazil. Ensnared by these oddball bubbles, Tufaile scoured the scientific literature and consulted with colleagues in search of clues. He got nowhere until one day in 1998, while searching the Web, he hit upon an amateur scientist's site. He then realized that those slow-go bubbles were not ordinary bubbles at all. They were tiny balls of water enclosed by microscopically thin shells of air, the whole package surrounded by water.

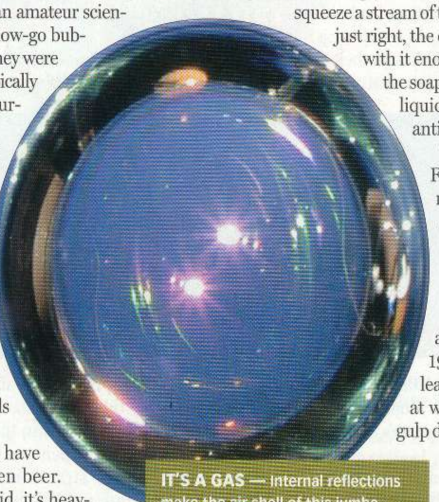
The eye-opening Web site, the work of engineer Chris T. Nadovich of Sellersville, Pa., described most of what was then known about structures called antibubbles, which was not much. It described them as the opposites of soap bubbles, which consist of air, enclosed by a film of liquid, immersed in air. Most antibubbles span less than a centimeter in diameter—although they have been made as big as racquetballs—and their air shells are about as wide as red blood cells.

To create antibubbles, enthusiasts have used various aqueous solutions, even beer. Because most of an antibubble is liquid, it's heavier and less buoyant than an ordinary air bubble, so it rises only sluggishly. Add some salt to the solution that ends up as the core, and an antibubble can become dense enough to sink.

In the past 70 years, scientists have occasionally toyed with antibubbles, more as a diversion than as a serious research pursuit. As people dabbled, they came up with a handful of names for the odd structures, including "negative bubbles" and "inverted bubbles."

In amateur circles, antibubble physics has flourished as a topic for kids' science fair projects. Meanwhile, adult aficionados have advanced the techniques of producing the intriguing globules. Nadovich and others spread the word about antibubbles through Internet sites and a chat room.

The era of mere dabbling may be coming to a close. Recently, antibubbles have begun attracting serious scientific scrutiny. High-speed video cameras and computers are enabling researchers to make unprecedented observations of the structures and behaviors of antibubbles. Some physicists have started exploring why antibubbles persist even though there's no obvious force keeping their fragile shells of air intact. A few investigators are even exploring the possibility that antibubbles could have practical uses, such as speeding up chemical reactions or forming a new kind of foam that might be useful as a lubricant or filtration material.



IT'S A GAS — Internal reflections make the air shell of this jumbo antibubble (shown twice actual size) look deceptively bulky. The shell's thickness is less than that of a human hair.

FRITZ

OUT OF THIN AIR Anybody who hand washes dishes has probably made antibubbles by the thousands, says foam physicist Stefan Hutzler of Trinity College in Dublin.

The most common way to make antibubbles is to first fill a glass and a squeezable bottle or bulb with a solution containing a mild soap. Next, holding the bulb a few millimeters above the solution squeeze a stream of the liquid into the glass. If this is done just right, the downward stream of liquid will drag with it enough air to envelope some droplets of the soap solution. Food coloring added to the liquid in the bulb makes it obvious that antibubbles are filled with that liquid.

Terry W. Fritz, an amateur scientist in Fort Collins, Colo., has taken this technique to the extreme. Using large tanks equipped with valves, pumps, and other plumbing, he routinely makes antibubbles 5 cm in diameter instead of the common 1-cm variety.

There are other ways of making antibubbles. For instance, in the late 1990s, Hutzler and his Trinity colleagues discovered that a vertical seam at which several soap films meet would gulp down a spherical droplet of soap solution and transform it, temporarily, into a football-shaped antibubble that descends while trapped in the seam. "It was like an ostrich swallowing an onion," Hutzler recalls.

A team of Australian and French researchers has recently gone a step beyond that. First, they set the stage by assembling three ordinary soap bubbles into what they call a raft. When they subsequently dribbled drops of soap solution onto the dimple where the three bubbles met, antibubbles of nearly identical sizes emerged into the underlying liquid beneath the raft.

"This is a foolproof way of making them," says Tim J. Senden of the Australian National University in Canberra, coleader of the work.

In 2002, Tufaile and José C. Sartorelli, also of the University of São Paulo, reported yet another method for making antibubbles.

They happened onto the technique in their investigations into chaotic phenomena, which include systems that range from a ball moving on a roulette wheel to weather patterns. Common to all of these is that slight changes in the starting conditions can create huge differences in their outcomes (*SN: 10/31/98, p. 285*).

While searching for hallmarks of chaos in the rates at which bubbles from a nozzle enter the bottom of a flask of a viscous glycerol solution, Tufaile found that bubbles often bumped into each other and coalesced. Then, a droplet of the viscous liquid sometimes punches through the surface of an ordinary bubble and gets coated by a shell of air. That event creates an antibubble.

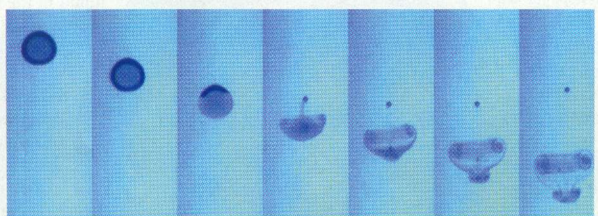
SHELL SHOCKED No matter how antibubbles are created, most of them have the same fate: They vanish in seconds. Recently, the first high-speed videos of popping antibubbles have revealed their demise in gory detail.

In a soap bubble, the enveloping film thins out at the top as gravity slowly pulls the fluid to the bottom of the bubble. Consequently, a soap bubble typically breaks at its uppermost surface unless a collision or other disruption shatters the film at some other location first.

In an antibubble, the process is inverted. The air in the shell tends to rise to the top of the antibubble, making the skin thinnest and most vulnerable at the bottom. In the Dec. 22, 2003 *New Journal of Physics*, an online publication, Stéphane Dorbolo, Hervé Caps, and Nicolas Vandewalle of the University of Liège in Belgium described video observations that confirm that an antibubble breaks from the bottom.

The video recordings also reveal how an antibubble's demise resembles that of its soap-bubble cousins. When punctured by a needle, an antibubble's air shell retracts like an overstretched elastic skin from the puncture point to the opposite side. There it coalesces into a tiny bubble that then shoots upward. Observations of popping soap bubbles similarly show the shell retracting, Dorbolo says.

Structural stability is one property in which soap bubbles and antibubbles seem to greatly differ. Although their skins are typically as thin as 10 nanometers—the equivalent of about 100 hydrogen atoms in a line—soap bubbles protected from evaporation and mechanical disruptions can be kept intact for months. In contrast, Fritz says his longest-lived antibubbles last a day.



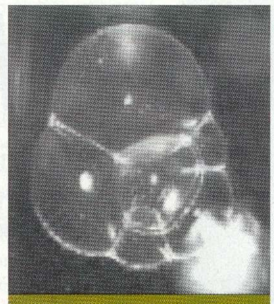
DEPTH CHARGE — A popping antibubble ejects its air shell as a tiny, rising bubble.

In a liquid film thinner than about 100 nm, intermolecular attractions called van der Waals forces tend to squeeze the film so much that it disappears with a pop, says Dorbolo. Yet, the electrical charges of atoms and molecules in the shell of a typical soap bubble and nature's tendency to increase entropy resist that squeezing.

In an antibubble, the van der Waals forces between the liquid molecules on either side of the air shell make them press against air shell. The relatively few molecules there can't mount much of a defense, says David Quéré of the Collège de France in Paris. So, antibubbles are expected to last only as long as it takes for air to migrate upward from the bottom portion of the shell.

Dorbolo and Vandewalle say they've conducted recent experiments that suggest that the antibubbles oppose van der Waals attractions with some counterforce, perhaps electrostatic repulsion, between detergent molecules that protrude into the air gap from the liquid on either side. The researchers have posted the details of their experiments on a Cornell University-hosted Web site where scientists and mathematicians share new findings (*www.arXiv.org/abs/cond-mat/0305126*).

FOLLOW THE LATHER As basic antibubble physics begins building momentum, some researchers are already looking toward applications. For example, if antibubbles can be stabilized, the odds of producing a long-lasting froth of them—an antifoam—go way up.



ALL WET — Antibubble-like structures composed of water surrounded by an oil shell form an unusual, all-liquid foam.

Antifoam might prove suitable for some uses not usually associated with foams. For example, it might act as a new type of lubricant—a foam analogy to ball bearings, speculates Hutzler.

Dorbolo imagines taking advantage of the web of thin passageways permeating the antifoam to develop a novel way to filter air or other gases.

So far, no one has made enough antifoam to test these ideas. When the Trinity team tried to make antifoams, it could assemble only five or six antibubbles before they popped, Hutzler says.

Tufaile claims to have made an antifoam containing 50 to 60 antibubbles, but these too were short-lived.

Even without a long-lasting antifoam, antibubbles may offer industrial potential, says C. Stuart Daw of Oak Ridge (Tenn.) National Laboratory. Compared with ordinary gas bubbles in a liquid, antibubbles provide twice the surface area through which exchanges of molecules or chemical reactions might take place. Also, because antibubbles rise relatively slowly, there's extra time for interactions with molecules on both sides of the gas shell.

This slowness, Daw says, "could have considerable benefits for chemical processes," such as removing smokestack pollutants and manufacturing chemicals and drugs.

Large antibubbles may have applications in the research laboratory as well, says physicist José Eduardo Wesfreid of the École Supérieure de Physique et de Chimie Industrielles in Paris. He notes that the arrangement of water molecules pressing on air in the shells of antibubbles at least a few centimeters in diameter probably breaks down when fingers of fluid poke into the interface. Studying that boundary-destroying interpenetration might offer new insights into how such layered structures break apart, he suggests. Although poorly understood, that type of breakdown, known as the Rayleigh-Taylor instability, is a major feature of many physical systems, ranging from dripping paint to supernovas, Wesfreid notes.

Replacing the air in antibubble shells with liquids opens yet other possibilities. Late last year, temporarily working with Quéré, Dorbolo created globules of water in an oil shell in water. Those have such great stability, Dorbolo says, that he has already made them into a kind of slimy antifoam, though he has yet to investigate the gunk's properties.

Tufaile says that he has made structures consisting of oil enclosed within an alcohol shell inside oil.

Some liquid-liquid antibubbles could be useful for drug delivery, adds Quéré. With antibubbles centering on a drug-containing solution surrounded by a shell of light-activated liquid-polymer precursors, a dose of ultraviolet light could harden the shell, creating sturdy, drug-packed capsules.

It remains to be seen whether such approaches will provide seeds of new technologies or be as transient as bubbles. ■

DORBOLO; DORBOLO ET AL./NEW JOURNAL OF PHYSICS