

Award Address

Strange Fizzical Attraction

2004 James Flack Norris Award, sponsored by the Northeastern Section of the ACS¹

by Richard N. Zare

Fizz and foam have spelled fun to me as long as I can remember. It was therefore a great pleasure to have the opportunity to present a talk on the subject at the November meeting of the Northeastern Section of the American Chemical Society. The title was “Chemical Fizzics: Seeing Chemistry in Action” and the occasion was my acceptance of the 2004 James Flack Norris Award for Outstanding Achievement in the Teaching of Chemistry. This presentation grew out of an earlier talk presented at Anchor Steam Brewery, San Francisco (see photograph below), and it can be found in all its glory (1 hour and 50 minutes) in streaming video on my Web site (1). The lecture is much too long to describe in detail. Nevertheless, I hope I might be permitted to explain briefly why I find bubbles so fascinating.

It is traditional to divide matter into three principal states—gases, liquids, and solids. A gas is said to take the shape of its container and to fill it; a liquid also takes the shape of a container but does not necessarily fill it; and a solid takes its own shape irrespective of the shape of the container. The density of a typical gas is 10^{19} molecules per cm^3 at STP, whereas that of a liquid or a solid is $\sim 10^{22}$ molecules per cm^3 . How should we then categorize the collection of bubbles called foam? From the viewpoint of density it is a gas. Foam closely follows the ideal gas law in terms of how its volume changes with pressure and temperature. But foam does not fill its container. Moreover, it can be readily poured from one container to another. In this sense foam is surely a liquid. Yet it can be cut with a knife or shattered by a quick

motion, and in this sense, foam is a solid. Substances that can assume the properties of each of the three principal states of matter are indeed strange—and so began my love affair with foam, fizz, and bubbles.

Commonly, one imagines that bubbles are child's play. Pictures abound showing children enchanted by blowing bubbles, so you might be surprised to find that bubbles do occupy an important place in contemporary technology (2). Let me cite just a few examples: the recovery of oil from tired oil wells in which bubbles are injected to help lift heavier crude to the surface, much as a raisin can be made to rise in a glass of champagne; cooking, in which the boiling of water is a key process for heat transfer (not to overlook its use in steam generation for energy production); and gas–liquid reactions that rely on bubbles to increase the contact area between the two phases. This last process actually leads to interesting chemical separations in which froth is used to achieve a partial separation of components in a mixture. For example, froth flotation is used extensively to separate minerals as well as to purify water. Recently, chemical engineers are working to apply froth flotation to separate and recover high-quality acrylonitrile butadiene styrene from mixed-plastics wastes generated from obsolete appliances so that the former can be recycled. In a more common example, taste the frothy head on a beer and compare that to the liquid. The foam is bitterer because it has extracted some of the bitter flavors of the hops from the beer. In turn, the rising foam has made the beer sweeter tasting—a little-known benefit of bubble power!

Affecting the Next Generation

Let me express my profound gratitude and pleasure in being selected by the Northeastern Section of the American Chemical Society for this great honor. Teaching and mentoring are both fairly private activities whose effectiveness is hard to judge, even by those most closely associated with the effort, and often only after the passage of much time! Yet, it is one of the most important activities we can do to renew the love of inquiry and spark the imagination of the next generation. I am mindful that many, many others are qualified—I daresay some more qualified than I—to receive this honor, and I accept it on the behalf of so many of us whose efforts usually go unmarked and unsung. Teaching and mentoring are so significant in preparing future chemists. I am grateful to the Northeastern Section for celebrating their importance.

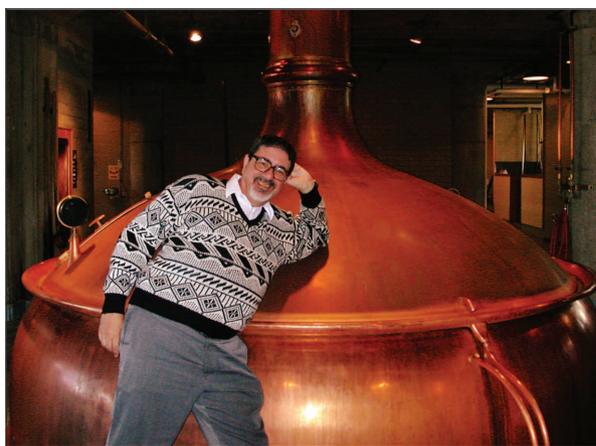


photo by Mara Taber

Figure 1. Richard Zare leaning against a large copper fermenter at Anchor Steam Brewery, San Francisco.

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Do bubbles in a liquid rise straight up? It is common experience to observe ascending bubbles in clear carbonated liquid, such as soda water, sparkling wine, and beer. The bubbles form on tiny irregularities on the surface of a container, and as they rise, they grow and accelerate. Neil Shafer-Ray and I studied that phenomenon many years ago and wrote a popular paper titled "Through a Beer Glass Darkly" in which we showed that this phenomenon was caused by nucleation. As the bubble rises, the bubble accretes more carbon dioxide gas inside it from the supersaturated liquid in contact with it, causing the bubble to swell in size and to accelerate its ascent (3). More recently, Andrew Alexander and I have reported that in some carbonated beverages, such as Guinness beer, the bubbles sink on the sides of the container while rising in the center during settling (4). Once launched, it might seem obvious that a single bubble would rise straight upward because its buoyancy force is directed opposite to that of gravity. This notion, however, is not completely correct! A bubble with a radius larger than about 0.7 mm oscillates in shape and undergoes zigzag motions as it rises. At still larger radii, this instability leads to bubble fission. This topic serves to introduce us to bubble hydrodynamics (5), a subject full of surprises and difficulties arising from the bubble's interaction with its own wake. When the liquid becomes turbulent or when many bubbles interact, the complications can be overwhelming. Simplifying approximations are needed. Finding the right approximation is a subject of extensive present-day research.

After formation and lift-off from the surface of the container, a bubble rapidly approaches a terminal velocity. Its terminal velocity is determined by the balance between the buoyant rise force of the lighter bubble compared to the heavier liquid, and the drag force that the bubble experiences, which depends on the shape and velocity of the bubble. (This last statement assumes that the liquid is not serving as a bubble chamber and we can neglect any effects of nucleation.) As the bubble rises, a new interface is created at the upstream hemisphere of the bubble. This interface flows toward the downstream hemisphere. At the interface, water molecules are on one side and gas molecules are on the other side. In addition, surfactant molecules may be present, and, if so, they will exert a marked influence on bubble motion and dynamics. The water molecules at the interface are continually exchanging with water molecules in the bulk fluid, and also with water vapor molecules in the gas (according to the equilibrium vapor pressure). This exchange results in the creation of a fresh interface at the upstream hemisphere. The result is that gas bubbles in pure water are self-cleaning as the interface is being continually renewed. This behavior, however, is in marked contrast to what happens when surfactants are dissolved in the water. The surfactant molecules accumulate at the water-gas interface of the bubble with the hydrophilic part of the surfactant pointing into the water and the hydrophobic part of the surfactant pointing into the gas of the bubble. The presence of a surfactant coating makes the bubble more rigid with less interface turnover.

This effect can provide a simple solution to a puzzle: Why do bubbles rise more rapidly in soda water than in champagne, and more rapidly in champagne than in beer? All three liquids have approximately the same viscosity. The answer to the puzzle is that the concentration of surfactants differs markedly in the three liquids—with soda water being nearly surfactant-free, champagne intermediate, and beer loaded with dissolved organic surfactants. We know that this concentration variation exists because soda water does not sustain bubbles on its surface, champagne does, and beer often forms a thick head of foam. In soda water, the clean bubble rises faster because its entire surface is mobile. The situation is very different for a bubble in surfactant-contaminated water. Surfactant molecules diffuse to the bubble surface where they accumulate at the interface and are pushed downward by the flow. Repulsion between surfactant molecules primarily in the downstream hemisphere counters the squeezing by the flow. Additionally, the flow is not uniform with the angle on the bubble; it increases from zero at the upstream pole stagnation point to a maximum near the equator, and decreases again to zero at the downstream pole. As a result, convection decreases toward both poles, causing the surfactant-coated bubble to rise more slowly than a clean bubble. The effect is astonishingly large. In soda water, bubbles rise something like a factor of two more rapidly than they do in beer.

This example shows the fine interplay between physics, chemistry, and chemical engineering that characterizes bubble research. It is in my opinion an excellent tool for introducing the young future chemist to this wondrous world we live in. I feel it is so important to teach students that nifty effects having a scientific basis surround us and are not just something made to happen occasionally in a laboratory.

Note

1. This paper is derived from a talk given at the presentation of the James Flack Norris Award for Outstanding Achievement in the Teaching of Chemistry of the Northeastern Section of the American Chemical Society, held November 11, 2004, at Massachusetts Institute of Technology.

Literature Cited

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4. Do bubbles in Guinness go down? See this mirror Web site <http://www.chem.ed.ac.uk/guinness/> and <http://www.stanford.edu/group/Zarelab/guinness/> (both sites accessed Feb 2005).
5. Bubble Hydrodynamics. <http://www.bubbleology.com/Hydrodynamics.html> (accessed Feb 2005).

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