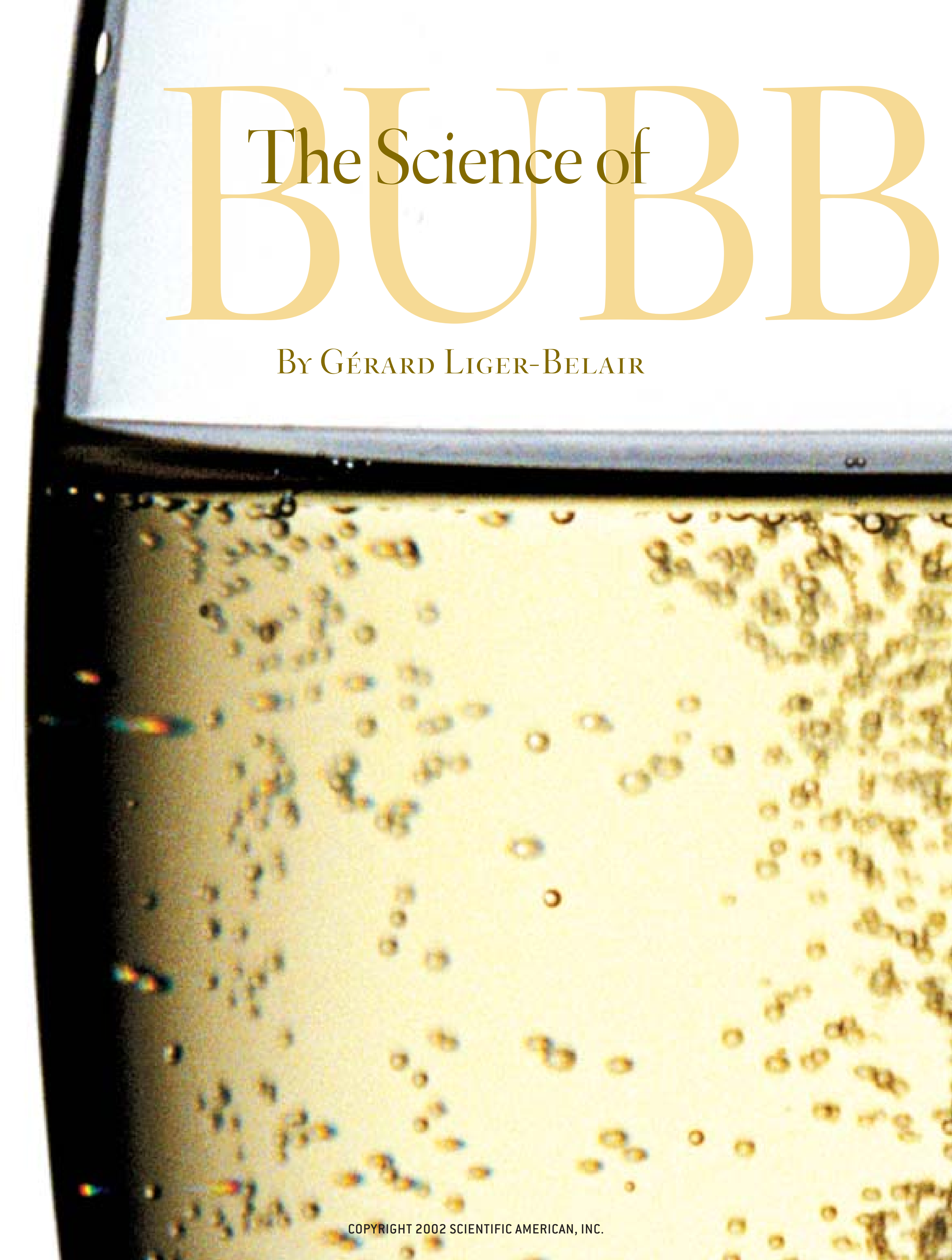
The Science of BUBB

By Gérard Liger-Belair



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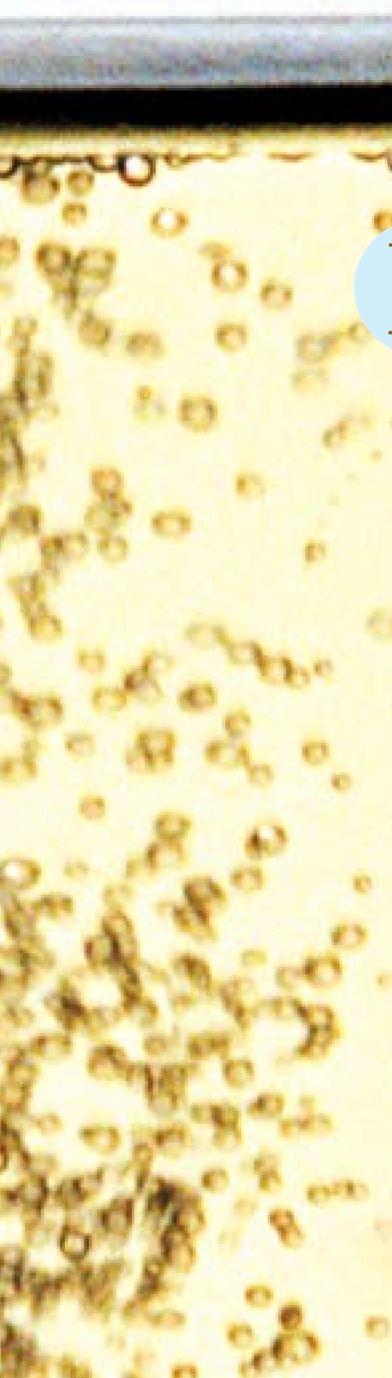
Scientists study the nose-tickling effervescence of champagne—an alluring and unmistakable aspect of its appeal



Pop open a bottle of champagne and pour yourself a glass. Take a sip. The elegant surface fizz—a boiling fumarole of rising and collapsing bubbles—launches thousands of golden droplets into the air, conveying the wine's enticing flavors and aromas to tongue and nostrils alike. A percussive symphony of diminutive pops accompanies the tasty mouthful, juxtaposing a refreshing carbonated chill and a comforting alcoholic warmth. Such is the enchantment of bubbly, the classic sparkling wine of northeastern France's Champagne district, a libation that has become a fixture at festive celebrations worldwide.

Among the hallmarks of a good champagne are multiple bubble trains rising in lines from the sides of a poured glass like so many tiny hot-air balloons. When they reach the surface, the bubbles form a ring, the so-called *collerette,* at the top of a filled flute. Although no scientific evidence correlates the quality of a champagne with the fineness of its bubbles, people nonetheless often make a connection between the two. Because ensuring the traditional effervescent personality of champagne is big business, it has become important for *champenois* vintners to achieve the perfect *petite* bubble. Therefore, a few years ago several research colleagues from the University of Reims Champagne-Ardenne and Moët & Chandon and I decided to examine the behavior of bubbles in carbonated

ON THE RISE: The short but spectacular ascent of champagne bubbles to the top of a glass embodies a complex physicochemical system that is both more functional and more picturesque than one might expect.

beverages. Our goal was to determine, illustrate and finally better understand the role played by each of the many parameters involved in the bubbling process. The simple but close observation of a glass filled with sparkling wine, beer or soda revealed an unexplored and visually appealing phenomenon. Our initial results concerned the three main phases of a bubble's life—birth, ascent and collapse.

Bubble Genesis

IN CHAMPAGNE, sparkling wines and beers, carbon dioxide is principally responsible for producing gas bubbles, which form when yeast ferments sugars, converting them into alcohol and carbon dioxide molecules. Industrial carbonation is the source of the fizz in soda drinks. After bottling or canning, equilibrium is established between the carbon dioxide dissolved in the liquid and the gas in the space directly under the cork, cap or tab, according to Henry's law. That law states that the amount of gas dissolved in a fluid is proportional to the pressure of the gas with which it is in equilibrium.

When the container is opened, the pressure of the gaseous carbon dioxide above the liquid falls abruptly, breaking the prevailing thermodynamic equilibrium. As a result, the liquid is supersaturated with carbon dioxide molecules. To regain a thermodynamic stability corresponding to atmospheric pressure, carbon dioxide molecules must leave the supersaturated fluid. When the beverage is poured into a glass, two mechanisms enable dissolved carbon dioxide to escape: diffusion through the free surface of the liquid and bubble formation.

To cluster into embryonic bubbles, however, dissolved carbon dioxide molecules must push their way through aggregated liquid molecules, which are strongly linked by van der Waals forces (dipole attraction). Thus, bubble formation is limited by this energy barrier; to overcome it requires supersaturation ratios higher than those that occur in carbonated beverages.

In weakly supersaturated liquids, including champagne, sparkling wines, beers and sodas, bubble formation requires preexisting gas cavities with radii of curvature large enough to overcome the nucleation energy barrier and grow freely. This is the case because the curvature of the bubble interface leads to an excess of pressure inside the gas pocket that is inversely proportional to its radius (according to Laplace's law). The smaller the bubble, the higher the overpressure within it. Below a critical radius, the pressure excess in a gas pocket forbids dissolved carbon dioxide to diffuse into it. In newly opened champagne, the critical radius is submicrometric, around 0.2 micron.

THE AUTHOR

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EISENHUT & MAYER *Getty Images* (*preceding pages and this page*); COURTESY OF GÉRARD LIGER-BELAIR (*insets*)

CHAMPAGNE BUBBLES

LIFE CYCLE OF A BUBBLE: The brief existence of a champagne bubble begins on a tiny mote of cellulose left clinging to the sides of a glass after it is wiped dry (*bottom*). When the sparkling wine is poured, a submicron-diameter gas pocket forms on the cellulose fiber. Dissolved carbon dioxide under pressure enters this small cavity and eventually expands it so much that buoyancy causes it to separate from the nucleation site. During its journey to the surface, the bubble enlarges further as more carbon dioxide makes its way in (*middle*). Simultaneously, aromatic flavor molecules in the beverage attach themselves to the gas/water membrane, a phenomenon that slows the bubble's ascent by boosting its drag. Soon after emerging at the surface, the flavor-carrying gas capsule collapses on itself and shoots a bit of the wine into the air, thus enhancing the champagne's smell and savor (*top*).

SHOW ME THE BUBBLES: Champagne is best served in a long-stemmed flute—a slender glass with a tulip- or cone-shaped bowl containing six ounces or more (*left*), say wine experts. The tall, narrow configuration of the flute extends and highlights the flow of bubbles to the crown, where the restricted open surface area concentrates the aromas carried up with the bubbles and released by their collapse. The slender stemware also prolongs the drink's chill and helps retains its effervescence.

The flute is better suited for drinking sparkling wine than the "champagne" coupe, the short-stemmed, saucer-shaped glasses that were once so fashionable (*see bottom of box on next page*). Legend has it that these glasses were originally modeled on the celebrated breasts of Marie Antoinette, queen of France in the late 18th century. Although it is still popular, the coupe was never designed for drinking champagne and thus does not allow the taster to fully enjoy its qualities, according to wine connoisseurs. Shallow and wide-brimmed, coupe glasses tend to be unstable and too likely to spill, and they fail to keep the wine as cold as tall wine flutes do. Further, coupes do not present the elegant bubble trains to best advantage.

To open a bottle of champagne, hold it with the cork pointed at a 45-degree angle upward, away from you or anyone else. Hold the cork and gently turn the bottle in one direction. Rather than popping off with a bang, the cork should come off with a subdued sigh. A loud pop wastes bubbles; as the saying goes, "The ear's gain is the palate's loss." *—G.L.-B.*

To observe bubble production sites (or "bubble nurseries") in detail, we aimed a high-speed video camera fitted with a microscope objective lens at the bases of hundreds of bubble trains. Contrary to general belief, these nucleation sites are not located on irregularities on the glass surface, which feature length scales far below the critical radii of curvature required for bubble formation. Bubble nurseries, it turns out, arise on impurities *attached* to the glass wall. Most are hollow and roughly cylindrical cellulose fibers that fell out of the air or remained from the process of wiping the glass dry. Because of their geometries, these exogenous particles cannot be wet completely by the beverage and are thus able to entrap gas pockets when a glass is filled [*see bottom illustration at left*].

During bubble formation, dissolved carbon dioxide molecules migrate into the minute gas pockets. Eventually a macroscopic bubble grows, which initially remains rooted to its nucleation site because of capillary forces. Finally the bubble's increasing buoyancy causes it to detach, providing the opportunity for a new bubble to form. The process repeats until bubble production ebbs because of a dearth of dissolved carbon dioxide.

Cyclic bubble production at a nucleation site is characterized by its bubbling frequency—that is, the number of bubbles produced per second, a figure that can be illustrated using a stroboscope. When the strobe's flash frequency equals that of bubble production, the bubble train appears frozen.

Because the kinetics of bubble growth depend also on the dissolved carbon dioxide content, bubble formation frequencies vary from one carbonated beverage to another. In champagne, for example, in which the gas content is approximately three times that of beer, the most active nucleation sites emit up to about 30 bubbles per second, whereas beer bubble nurseries produce up to only about 10 bubbles per second.

Bubble Ascent

AFTER A BUBBLE is released from its nucleation site, it grows as it makes its way to the surface [*see middle illustration at left*]. Bubble enlargement during ascent is caused by a continuous diffusion of dissolved carbon dioxide through the bubble's gas/liquid interface. Buoyancy increases as bubbles expand, causing them to accelerate continuously and separate from one another on the way up.

Beers and sparkling wines are not pure liquids. In addition to alcohol and dissolved carbon dioxide, they contain many other organic compounds that can display surface activity like that of a soap molecule. These surfactants, comprising mostly proteins and glycoproteins, have a water-soluble and a water-insoluble part. Rather than staying dissolved in the bulk liquid, surfactants prefer to gather around the surface of a bubble with their hydrophobic ends aimed into the gas and their hydrophilic ends stuck in the liquid.

The surfactant coating around a bubble becomes crucial to its behavior when growing buoyancy induces detachment and forces the gas pocket to plow its way through the intervening liquid molecules. Adsorbed surfactant molecules stiffen a bubble by forming something like a shield on its surface. According to fluid dynamical theory, a rigid sphere rising through a fluid runs into greater resistance than a more flexible sphere with a surface free of surfactants. In addition, surfactant molecules encountered during ascent gradually collect on the bubble surface, enlarging its immobile area. Therefore, the hydrodynamic drag experienced by a rising bubble of fixed radius increases progressively; the bubble slows to a minimum velocity when the gas/liquid interface becomes totally contaminated. Strictly speaking, the complete rigidification of the bubble boundary occurs before it is completely covered by surfactants, as recently demonstrated by a French team from Louis Pasteur University in Strasbourg.

The behavior of rising, expanding bubbles is more complex than that of those with fixed radii. In the former instance, a bubble's volumetric expansion during its ascent through the supersaturated liquid causes its surface area to grow, offering greater space for surfactant adsorption. Swelling bubbles are consequently subject to opposing effects. If the dilation rate overcomes the speed with which surfactants stiffen the surface, a bubble "cleans" its interface constantly because the ratio of the surface area covered by surfactants to that free from surface-active agents decreases. If this ratio increases, the bubble surface becomes inexorably contaminated by a surfactant monolayer and grows rigid.

By measuring the drag coefficients of expanding champagne and beer bubbles during their journeys up to the surface and then comparing them with data found in the scientific literature of bubble dynamics, we concluded that beer bubbles act very much like rigid spheres. In contrast, bubbles in champagne, sparkling wines and sodas present a more flexible interface during ascent. This is not overly surprising, as beer contains much higher quantities of surfactant macromolecules (on the order of several hundred milligrams per liter) than does champagne (only a few mg/L). Furthermore, because the gas content of beer is lower, growth rates of beer bubbles are lower than those of champagne bubbles. As a result, the cleaning effect caused by a beer bubble's expansion may be too weak to avoid rigidification of its gas/liquid interface. In champagne, sparkling wines and sodas, bubbles grow too rapidly and there are too few surfactant molecules for them to become stiff.

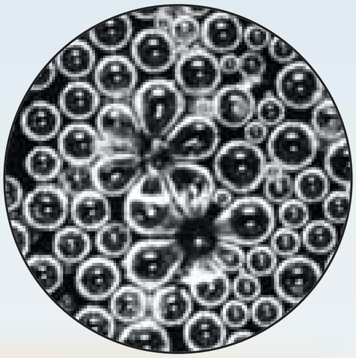
Bubble Collapse

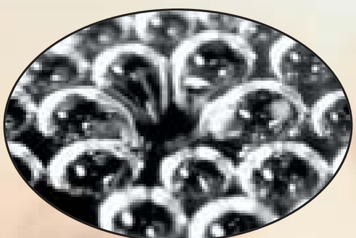
IN THE SEVERAL SECONDS after its birth and release, a bubble travels the few centimeters to the beverage's surface, eventually reaching a diameter of about a millimeter. Like an iceberg, a gas bubble at the top of a drink emerges only slightly from the liquid, with most of its volume remaining below the surface. The emerged part, the bubble cap, is a hemispherical liquid film that gets progressively thinner as a result of drainage around the sides. When a bubble cap reaches a certain critical thickness, it becomes sensitive to vibrations and thermal gradients, whereupon it finally ruptures. Working independently in 1959, two physicists, Geoffrey Ingram Taylor of the University of Cambridge and Fred E. C. Culick of the California Institute of Technology, showed that surface tension causes a hole to appear in the bubble cap and that the hole propagates very quickly. For bubbles of millimeter size, this disintegration takes from 10 to 100 microseconds [*see sequence at right*].

After the bubble cap breaks, a complex hydrodynamic process ensues, causing the collapse of the submerged part of the bubble. For an instant, an open cavity remains in the liquid surface. Then the inrushing sides of the cavity meet and eject a high-speed liquid

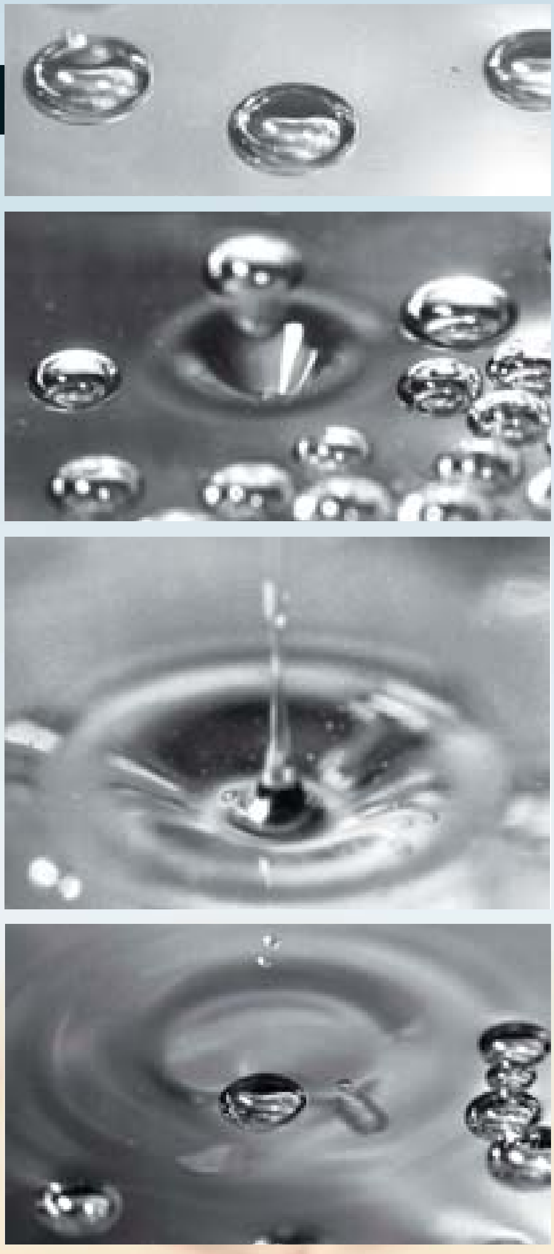
DEATH OF A BUBBLE

POP GOES THE BUBBLE: The collapse of a champagne bubble begins nearly as soon as it breaches the surface of the beverage [*sequence at right*]. In the second image, the thin liquid film that constitutes the emerged part of the bubble has just ruptured. During this extremely brief event, the shape of the bubble—nearly a millimeter wide—remains intact. The collapse of the cavity gives rise to a high-speed liquid jet that flies above the surface [*third image*]. Because of its own velocity, this jet becomes unstable, forming a capillary wave that breaks up the flow into droplets. Hundreds of bubbles are bursting every second after pouring, so the liquid surface is literally spiked with cone-shaped structures, unfortunately too short-lived to be seen with the naked eye.





BUBBLE FLORETS: Because the collapse of surface bubbles is very rapid (less than 100 microseconds), few photographs capture the process. But clusters of champagne bubbles form visually appealing flower-shaped structures [*left*] when they are deformed by the sucking force created by a nearby popped bubble. The bubble caps adjacent to the bubble-free central zones are stretched toward the now empty cavities.



TOSHIO NAKAJIMA *Photonica*; COURTESY OF GÉRARD LIGER-BELAIR (*insets*)

jet above the free surface. Because of its high velocity, this jet becomes unstable, developing a capillary wave (the Rayleigh-Plateau instability) that fragments it into droplets called jet drops. The combined effects of inertia and surface tension give the detaching jet drops a variety of often surprising shapes. Finally they take on a quasi-spherical shape. Because hundreds of bubbles are bursting each second, the beverage surface is spiked with transient conical structures, which are too short-lived to be seen with the unaided eye.

Aroma and Flavor Release

BEYOND AESTHETIC considerations, bubbles bursting at the free surface impart what merchants call "feel" to champagne, sparkling wines, beers and many other beverages. Jet drops are launched at several meters per second up to a few centimeters above the surface, where they come in contact with human sense organs. Nociceptors (pain receptors) in the nose are thus stimulated during tasting, as are touch receptors in the mouth when bubbles burst over the tongue; this bursting also yields a slightly acidic aqueous solution.

In addition to mechanical stimulation, bubbles collapsing at the surface are believed to play a major role in the release of flavors and aromas. The molecular structures of many aromatic compounds in carbonated beverages show surface activity. Hence, bubbles rising and expanding in the bulk liquid serve as traps for aromatic molecules, dragging them along on their way up. These molecules concentrate at the surface. Bursting bubbles are thus thought to spray into the air clouds of tiny droplets containing high concentrations of aromatic molecules, which emphasize the flavors of the beverages. Our future research plans include quantifying this flavor-release effect for each of the numerous aromatic molecules in champagne.

Contrary to what we had first thought, effervescence in carbonated beverages turned out to be a fantastic tool for investigating the physical chemistry of rising, expanding and collapsing bubbles. We hope readers will never look at a glass of champagne in quite the same way. SA

NATIONAL GEOGRAPHIC CHANNEL

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MORE TO EXPLORE

Through a Beer Glass Darkly. Neil Shafer and Richard Zare in *Physics Today,* Vol. 44, pages 48–52; 1991.

Beauty of Another Order: Photography in Science. Ann Thomas. Yale University Press, 1997.

The Secrets of Fizz in Champagne Wines: A Phenomenological Study. Gérard Liger-Belair et al. in *American Journal of Enology and Viticulture,* Vol. 52, pages 88–92; 2001.

Kinetics of Gas Discharging in a Glass of Champagne: The Role of Nucleation Sites. Gérard Liger-Belair et al. in *Langmuir,* Vol. 18, pages 1294–1301; 2002.

Physicochemical Approach to the Effervescence in Champagne Wines. Gérard Liger-Belair in *Annales de Physique,* Vol. 27, No. 4, pages 1–106; 2002.