THROUGH A BEER GLASS DARKLY

Although many of us think of beer as an enjoyable after-work refreshment, others consider the physics and chemistry of beer to be serious—well, mostly serious—business.

Neil E. Shafer and Richard N. Zare

Pour yourself a glass of beer and look closely at the rising bubbles. Careful examination shows that they are seldom distributed uniformly throughout the liquid. Instead, streams of bubbles appear to rise from certain spots on the surface of the glass. Closer inspection reveals that the bubbles rapidly grow in size as they ascend, the volume of each bubble often doubling or more by the time it reaches the top of the glass. In addition, the speed of the bubbles increases as they travel upward.

You might think that in the several millennia that beer has been with us we would have already learned all there was to know about this curious brew. Yet a glass of beer reveals a remarkable interplay among gases, liquids and solids, temperature, pressure and gravity—an interplay that is still not completely understood. Once you begin to learn about the nature of beer bubbles you will never again look at a glass of beer in quite the same way.

Fresh beer will go flat in an open container as the carbon dioxide produced during fermentation escapes into the atmosphere. To prevent this, beer is kept in sealed bottles or cans so that the CO_2 is trapped. Some CO_2 molecules collect under the cap or lid, until the pressure inside the container reaches two or three times the pressure of the atmosphere. Other CO_2 molecules remain "free floating" (dissolved) in the beer below. Under these conditions an equilibrium is established between the dissolved and gaseous CO_2 . The colder the beer, the more CO_2 molecules are dissolved in the liquid. Pop off the cap from a beer bottle or pull the tab on a beer can and—fizz—trapped CO_2 gas rushes out. The equilibrium is broken.

Pour the beer into a glass and bubbles appear. But how do these tiny gas pockets form? Visible bubbles begin as invisible clusters or microbubbles of CO₂ molecules that grow on rough spots, called "nucleation sites," where the CO₂ molecules can attach themselves and

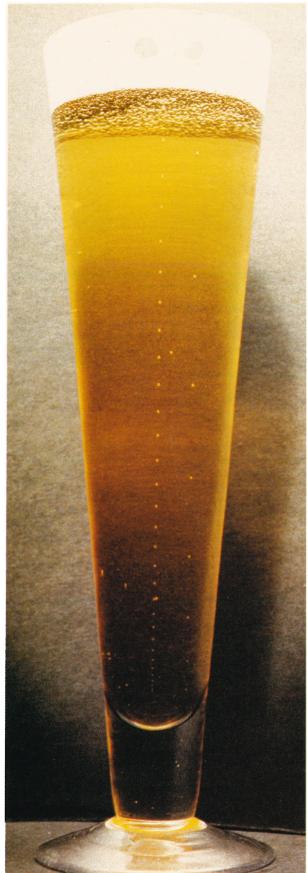
Neil Shafer is a postdoctoral research associate and **Richard Zare** is Marguerite Blake Wilbur Professor of Chemistry in the department of chemistry at Stanford University.

coalesce. In fact, the formation of beer bubbles is very similar to the formation of rain clouds, in which rain droplets grow on dust particles.1 Indeed, we can promote the bubbling of beer by introducing artificial nucleation centers such as grains of sugar, salt or pepper (ugh!), just as Donald Glaser introduced elementary particles into a bubble chamber to leave a track of nucleation centers.2 Before succeeding with the superheated diethyl ether bubble chamber, Glaser half-seriously tried out his bubble-chamber ideas by opening bottles of beer, ginger ale and soda water in the presence of a radioactive source. In the most impressive of a series of recent experiments at the University of California at Berkeley's Bevatron, Frank Crawford³ introduced 2×10^7 Fe²⁶⁺ particles with energies of 600 MeV/nucleon into a glass of beer every 4 seconds to try once more to find ionizing-particle-induced beer bubbling. No bubbles were found.

Instead of relying on foreign particles to start beer bubbling, we can let the surface of the glass provide nucleation sites. At rough patches or microcracks on the surface, where CO_2 molecules have a chance to accumulate, bubbles form. Often one sees whole strings of bubbles streaming gracefully upward from these nucleation sites. (See figure 1 and the cover photo.)

Rapidly growing bubbles

But what makes bubbles grow as they rise? One might suppose that the drop in hydrostatic pressure as the bubble floats upward accounts for this behavior. Recall, however, that some of the bubbles double in size as they ascend. If a drop in pressure were responsible for this bubble growth, the pressure on a bubble at the bottom of the glass would have to be twice as great as the pressure on a bubble near the top—that is, 2 atmospheres rather than 1. But a bubble would have to rise roughly 30 feet for the pressure to drop this much. Thus the pressure-change hypothesis is wrong for a 12-ounce glass of beer. The correct explanation for bubble growth is that bubbles accumulate carbon dioxide as they ascend through the beer. In other words, bubbles act as nucleation centers for themselves.



Bubbles in a glass of beer appear to rise in streams from spots on the surface of the glass. As they ascend, the bubbles grow larger and spread further apart. **Figure 1**

After a bottle of beer is opened, the partial pressure of dissolved CO_2 in the beer is greater than the pressure of the CO_2 in the bubble, and the dissolved gas travels from the beer to the bubble. Because this pressure difference remains almost constant, we expect (to a good approximation) the rate of bubble growth to be proportional to the surface area of the bubble:

$$\frac{\mathrm{d}N_{\mathrm{bubble}}}{\mathrm{d}t} = \gamma(4\pi r^2) \tag{1}$$

where $N_{\rm bubble}$ is the number of ${\rm CO_2}$ molecules in the bubble, γ is a proportionality constant, and $4\pi r^2$ is the surface area, based on the assumption that the bubble is a sphere of radius r. The simple form of equation 1 is valid only because the beer maintains the bubble at constant temperature and the atmosphere maintains the bubble at a constant pressure (the hydrostatic pressure of the beer being negligible).

Assume the CO₂ in a beer bubble obeys the ideal gas law, so that $P_{\rm bubble}$ $V_{\rm bubble}$ = $N_{\rm bubble}$ $k_{\rm B}$ $T_{\rm bubble}$, where $k_{\rm B}$ is the Boltzmann constant and $P_{\rm bubble}$, $V_{\rm bubble}$ and $T_{\rm bubble}$ are the pressure, volume and temperature of the bubble. Because $P_{\rm bubble}$ and $T_{\rm bubble}$ are constant, we can differentiate both sides of the ideal gas law with respect to time to find

$$\frac{\mathrm{d}N_{\text{bubble}}}{\mathrm{d}t} = \left(\frac{P_{\text{bubble}}}{k_{\text{B}}T_{\text{bubble}}}\right) \frac{\mathrm{d}V_{\text{bubble}}}{\mathrm{d}t}$$

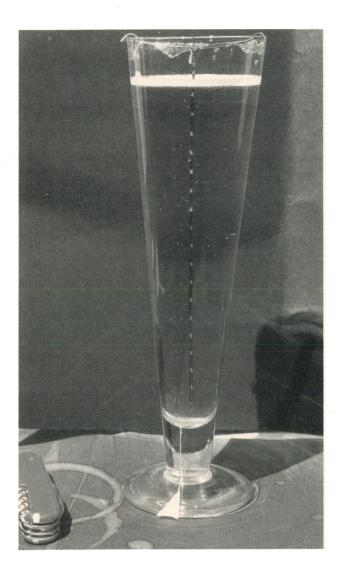
$$= \left(\frac{P_{\text{bubble}}}{k_{\text{B}}T_{\text{bubble}}}\right) 4\pi r^{2} \frac{\mathrm{d}r}{\mathrm{d}t} \tag{2}$$

If we set equation 1 equal to equation 2, we can solve the resulting first-order differential equation to find that

$$r = r_0 + v_r t \tag{3}$$

where $\rm r_0$ is the initial radius of the bubble and $v_r=\gamma k_{\rm B}\,T_{\rm bubble}/P_{\rm bubble}$ is the rate of increase of the bubble's radius.

The stream of beer bubbles shown in figure 2 provides



Notched copper wire suspended in a glass of beer allows measurement of the bubbles' radii from an enlarged photograph. Figure 2

 0.018 ± 0.004 cm and that the radius of the bubble grew at a rate v_r of 0.004 ± 0.001 cm/sec.

Buoyancy versus drag

What causes a bubble to rise? The answer of course is that the density of a CO_2 bubble is less than the density of the surrounding beer. The buoyancy force F_b is proportional to the volume of the beer displaced by the spherical bubble (Archimedes' principle):

$$F_{\rm b} = V_{\rm bubble}(\rho_{\rm beer} - \rho_{\rm bubble})g$$
 (4)

$$\approx V_{\text{bubble}} \rho_{\text{beer}} g$$
 (5)

where $V_{\rm bubble}$ is the volume of the bubble, $\rho_{\rm beer}$ is the density of the beer, $\rho_{\rm bubble}$ is the density of the CO₂ gas in the bubble, and $g=980~{\rm cm/sec^2}$ is the acceleration caused by gravity. In equation 5 we use the approximation that the density of the CO₂ gas is much less than that of the beer. If we also assume that the bubble moves slowly enough and is small enough that its shape remains spherical, we can relate the buoyancy force to the radius of the bubble:

$$F_{\rm b} \approx \frac{4\pi r^3}{3} \rho_{\rm beer} g$$
 (6)

As a bubble rises, it encounters resistance, or drag. In general, the drag on a rising bubble is a complicated function of its radius and speed dz/dt as well as of the viscosity, density and surface tension of the liquid it is in. If the ascending bubble had a fixed size, it would reach a constant, or terminal, velocity at which the buoyancy force exactly counterbalanced the drag force. But because the bubble's radius is always increasing, the drag force, which increases less rapidly than r^3 , can never quite catch up to the buoyancy force, which is proportional to r^3 . In other words, the upward buoyancy force increases more quickly than the downward drag force, causing the bubble to accelerate. This explains why in a stream of bubbles rising from a nucleation site on the beer glass, the bubbles near the bottom are smaller, slower and more closely spaced than those near the top, as is evident in the cover photo and figure 1.

To predict the motion of the beer bubble, we write

$$M_{\text{bubble}} \frac{\mathrm{d}^2 z}{\mathrm{d}t^2} = F_{\mathrm{b}} + F_{\mathrm{d}} \left(\frac{\mathrm{d}z}{\mathrm{d}t}, r \right)$$
 (7)

where $F_{\rm d}$ is the drag on the bubble and $M_{\rm bubble}$ is the sum of the bubble's mass $(4\pi r^3/3)\rho_{\rm bubble}$ and the mass of the

data for a wonderful test of our bubble-growth model. At the origin of the stream, CO_2 molecules collect at a nucleation site until the resulting bubble reaches a critical size and is able to break away. As soon as a bubble is released, another one starts to form. Because each bubble undergoes the same formation process, the bubbles are released at roughly equal time intervals. By measuring how long it takes for a number of bubbles in the string to reach the top of the glass, the time between adjacent bubbles can be calculated in absolute terms. For the stream pictured in figure 2 we observed that 107 ± 4 bubbles reached the top of the beer in 58 seconds, indicating that a bubble was released from the nucleation site every 0.54 ± 0.02 seconds.

Care must be taken in studying the size and shape of beer bubbles. Because the beer and glass act as a lens distorting the images of objects viewed through them, the bubbles are actually smaller than they appear. To compensate for this distortion, we placed next to the stream of bubbles a copper wire 0.26 cm in diameter and notched every 1.02 cm, and then photographed the bubbles. We measured the height of the bubbles z(t) with respect to the notches in the wire; we measured the radius r(t) of the bubbles by enlarging the photograph and comparing the horizontal width of the bubbles to the width of the wire. (See the table on page 51.) A linear fit to these data (plotted in figure 3) indicates that r_0 was equal to

liquid the bubble carries with it as it rises. By replacing $F_{\rm b}$ by equation 6 and assuming that the inertial force on the bubble $M_{\rm bubble}({\rm d}^2z/{\rm d}t^2)$ is much less than either the buoyancy force $F_{\rm b}$ or the drag force $F_{\rm d}$, we obtain the following differential equation for z(t):

$$F_{\rm d}\left(\frac{{\rm d}z}{{
m d}t}, v_r t + r_0\right) = \frac{-4\pi(v_r t + r_0)^3}{3}\rho_{\rm beer}g$$
 (8)

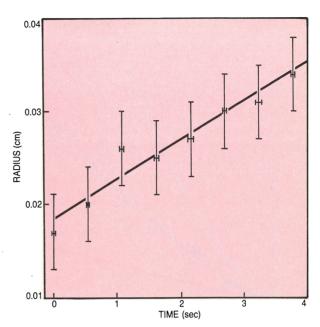
A solution of equation 8 for z(t) is independent of the initial velocity of the bubble. Just as in the case of a marble falling to the bottom of a jar of molasses, the trajectory of a rising beer bubble is almost independent of the initial velocity of the bubble. In the case of a marble in molasses, the velocity almost immediately assumes a constant value, whereas in the case of a beer bubble, the velocity almost immediately assumes a functional form that is dependent only on the bubble's radius.

Because it is so difficult to determine the theoretical drag $F_{\rm d}$ on a particle moving in a viscous medium, to predict the motion of such a particle we must rely on empirically determined correlations. These correlations are customarily made between various dimensionless parameters, the most familiar of which is the Reynolds number R, the ratio of inertial to viscous forces on the bubble. For a spherical bubble of radius r rising in beer of viscosity $\eta_{\rm beer}$ and density $\rho_{\rm beer}$, the Reynold's number is equal to $(2r\rho_{\rm beer}/\eta_{\rm beer})({\rm d}z/{\rm d}t)$. After measuring the beer's viscosity $(\eta_{\rm beer}=1.30\pm0.05~{\rm cP})$ and density $(\rho_{\rm beer}=1.00\pm0.02~{\rm g/cm^3})$, one can obtain an approxima-

Beer bubble statistics

Time <i>t</i> _n (sec)	Radius r _n (cm)	Height z, (cm)	Reynolds number <i>R</i> †
0.00	0.017 ± 0.004	0.0 ± 0.2	6.0 ± 2
0.54 ± 0.02	0.020 ± 0.004	1.2 ± 0.2	12 ± 3
1.08 ± 0.03	0.026 ± 0.004	3.4 ± 0.2	13 ± 3
1.62 ± 0.03	0.025 ± 0.004	5.2 ± 0.2	13 ± 3
2.16 ± 0.04	0.027 ± 0.004	7.0 ± 0.2	20 ± 4
2.70 ± 0.04	0.030 ± 0.004	9.6 ± 0.2	24 ± 4
3.24 ± 0.05	0.031 ± 0.004	12.4 ± 0.2	25 ± 4
3.78 ± 0.05	0.034 ± 0.004	15.6 ± 0.02	31 ± 4‡

[†]For a given set of experimental data points t_n , r_n and z_n , R is assumed to be $2\rho_{\text{beer}}r_nv_n/\eta_{\text{beer}}$, where $v_n=(z_{n+1}-z_n)/(t_{n+1}-t_n)$.



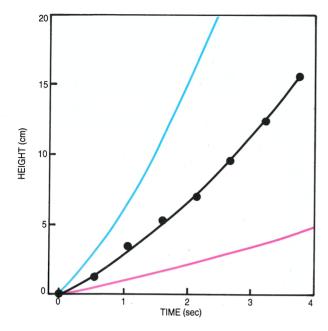
Radius of a rising beer bubble changes as a function of time. The smooth line is the best fit of the radius to $r = r_0 + v_r t$, where v_r is the rate of increase of the radius. The fit gives $r_0 = 0.018 \pm 0.004$ cm and $v_r = 0.004 \pm 0.001$ cm/sec. The error bars represent one standard deviation. The large uncertainty for r is caused by the finite resolution of the photographic process used in the technique for measuring the radius. **Figure 3**

tion for the Reynolds number of a rising beer bubble. We see from the table on this page that the rise of a beer bubble in a typical glass occurs at low to moderate Reynolds numbers (R < 50).

Although there is no simple solution for the expected drag on a beer bubble, it is instructive to assume that a beer bubble can be modeled as a slowly growing rigid sphere. Surprisingly, the drag on a rigid sphere is not a solved problem. Thus, we must rely on a large body of experimental data that is well known to the fluid dynamics community but perhaps less well known to most beer drinkers. The rates at which spherical objects of different radii and mass move through media of different viscosity and density have been fit to a standard drag curve, 5 which relates the Reynolds number of a rigid sphere flowing in a liquid to the so-called drag coefficient $C_{\rm d}=2F_{\rm d}/\pi\rho v^2r^2$. When one obtains a value for $F_{\rm d}$ from the standard drag curve and includes it in equation 8, the resulting firstorder differential equation for z can be solved numerically. Our measured values for z(t) agree with this solution when the initial value r_0 of the radius is taken to be 0.0143 cm and the rate of bubble growth v_r is taken to be 0.0042 cm/sec, in agreement with the values for r_0 and v_r we measured directly from the photograph.

Figure 4 shows that the rigid-sphere model for beer bubble effervescence is an excellent one for the small bubbles seen in a glass of beer. One may wonder whether it is necessary to rely on empirical methods (such as the standard drag curve) to fit the data. Figure 4 also shows the predicted z(t) for two analytical approximations to $F_{\rm d}$, Stokes's law and Oseen's law: Neither one reproduces our observations. If the beer bubble had a chance to grow just

 $[\]ddagger v_n$ is taken to be $(z_n - z_{n-1})/(t_n - t_{n-1})$.



a little larger, as it would on a journey to the top of a pitcher, then even the rigid-sphere model would be expected to break down. The rigid-sphere model is expected to underestimate the drag on such a rapidly moving bubble.

Foam: More than meets the eye

To understand why a beer bubble would rise more slowly than expected from the rigid-sphere model, we must examine the bubble after it has reached the surface of the beer. At the top of the glass, beer bubbles collect in a foam, called a head, which many beer drinkers will tell you never lasts long enough, while others argue that it lasts too long. For brewers the appearance and staying power of the head are often extremely important. In pure water, bubbles burst almost immediately on reaching the surface. whereas at the beach you will see foamy whitecaps on ocean waves. Whitecaps are caused primarily by the presence of a film of organic matter on the ocean's surface. Some beer manufacturers take the hint from nature and fatten the foam by adding surfactants to their beer. As it turns out, these and naturally occurring surfactants in beer significantly influence the dynamics of beer bubble effervescence. Thus the actual trajectory of a beer bubble is a complex matter.

It has been observed that the presence of even a small amount of surfactant significantly reduces the terminal velocity of an air bubble in water.⁶ Surfactants affect the ascent of a bubble by forming a rigid wall around the bubble, eliminating the lubricating effect of the circulation of the gas in the bubble; by causing enhanced boundary-layer separation, larger wakes and earlier vortex shedding; and by reducing the surface tension of the liquid, allowing the bubble to distort more easily from a spherical to an ellipsoidal shape.⁵ Not all of these effects operate in the same direction, but the net result is to slow the ascent of the bubble with respect to the prediction of the rigid-sphere model.

No one has quantitatively described the flight of a beer bubble from first principles, but a qualitative picture of the rise of a growing bubble is available.⁵ When the bubble is very small it is indeed spherical, but when it reaches a radius of 0.03 cm, it becomes ellipsoidal, with the major axis horizontal. Bubbles in a beer glass are usually

Height of a bubble in a glass of beer as a function of time, as determined from an enlarged version of figure 2. The data points are roughly one standard deviation in size. The black curve is the expected trajectory of a beer bubble if one assumes that the drag force $F_{\rm d}$ follows that of a rigid sphere with $r_0=0.0143$ cm and $v_r=0.0042$ cm/sec. If one assumes the same values for r_0 and v_r but that the drag force follows either Stokes's law $F_{\rm d}=6\pi\rho v_z r$ (blue) or Oseen's law $F_{\rm d}=6\pi\rho v_z r(1+3)_{16}R)$ (red), the calculated trajectories do not match the observed ones. **Figure 4**

so small that this effect does not play an important role. (If they appear ellipsoidal, it is most likely caused by the lensing effect of the glass.) If the radius of the bubble grew to roughly 0.1 cm—as it could in a "yard" of ale—the bubble would have reached a critical size at which its radius would begin to oscillate in time. It is believed that such oscillations are driven by the interaction of a bubble with its wake as the wake is shed. The oscillating bubble no longer ascends in a straight line but instead travels in a zigzag or helical path. While the bubble oscillates, its velocity increases very little with increasing radius. The onset of oscillations in bubble flow is accompanied by a sharp increase in the drag on the bubble. For an air bubble in pure water, the terminal velocity of a 1.3-mm bubble is actually greater than that of a 2.0-mm bubble because the 2.0-mm bubble oscillates.⁵ If the radius were to approach 1.0 cm—as it could in, say, a 5-m-deep fermenting vessel-the bubble would deform into a spherical cap, flat on the bottom and rounded on the top. A bubble of this size would be expected to exhibit a Rayleigh-Taylor instability and break apart.

The deformation, oscillation, wandering and ultimate breakup of a rising, rapidly growing bubble make beer bubble dynamics a rich phenomenon, worthy of study in the laboratory as well as in the pub. Well, here's suds in your eye. Bottoms up!

We thank David L. Huestis for first interesting us in the rise and fall of beer bubbles. We are also grateful to Andreas Acrivos and George M. Homsy for helping us to comprehend some of the subtle features of fluid mechanics and for keeping us from going astray.

References

- 1. C. F. Gohren, Clouds in a Glass of Beer: Simple Experiments in Atmospheric Physics, Wiley, New York (1987).
- D. A. Glaser, in Les Prix Nobel en 1960, Imprimerie Royal, Stockholm (1961), p. 77.
- 3. F. S. Crawford, Am. J. Phys. 58, 1033 (1990).
- 4. J. Walker, Sci. Am., December 1981, p. 172.
- See R. Clift, J. Grace, M. Weber, Bubbles, Drops and Particles, Academic, New York (1978).
- See A. M. Gaudin, Flotation, 2nd ed., McGraw-Hill, New York (1957).