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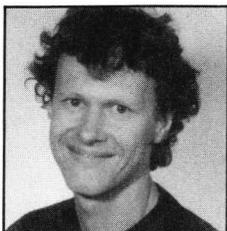
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Quenching a Thirst with Differential Equations

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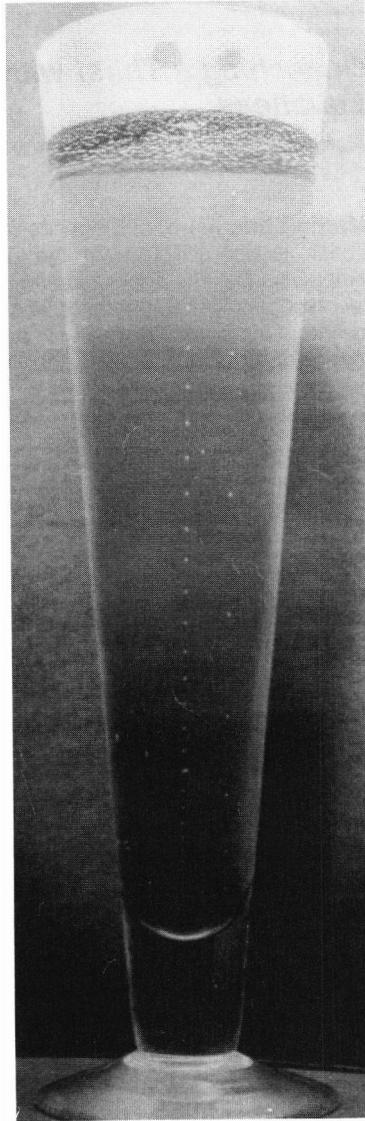
Most of us think of beer as an effervescent beverage designed to quench one's thirst. Yet this popular drink contains mathematical mysteries that can cause a differential equations class to bubble with interest. Can we model the behavior of CO_2 bubbles as they grow and rise in a glass of beer?

A Physical Model

Albert Einstein once said that one should make things as simple as possible, but not simpler. This is the guiding principle for the physical model we shall develop for the motion of the bubbles in a glass of beer. Observation tells us that bubbles of carbon dioxide form at certain sites in the bottom of the glass and rise to the top due to their buoyancy. Of course the bubbles are slowed down on their way by the resistance of the viscous liquid. It is a straightforward exercise to show that if the resistance were simply proportional to the speed of the bubbles, their speed would approach a constant "terminal velocity." Real bubbles, however, accelerate as they rise (see Figure 1 on page 414). Moreover, their diameter visibly increases, approximately doubling during their short trip to the surface.

We are forced to create a subtler model. A bubble's growth takes place through its surface; we assume that the rate at which molecules of CO_2 pass from the beer into a bubble is proportional to the bubble's surface area. This assumption accounts for the acceleration of the bubbles, since the larger a bubble becomes the greater will be the buoyant force making it rise. (Of course the drag on the bubble also increases with the bubble size, but the buoyancy increases in proportion to the volume—the cube of the radius—while the drag should be proportional to the radius or perhaps the square of the radius. Thus as a bubble grows its buoyancy will increase faster than the drag; hence the bubble will accelerate.)

We should also consider the added bubble growth due to the decrease in pressure acting on the bubbles as they near the surface. The relationship between the pressure, volume, amount of CO_2 , and temperature in a bubble is assumed to be given by the "ideal gas" equation $PV = nRT$, in which we will assume that the temperature T remains that of the surrounding beer, a constant during the bubble's brief trip.



By permission of the American Institute of Physics and R. N. Zare [1].

Figure 1

Very smooth (Reynolds number < 1) flow with speed v of a fluid around a solid sphere of radius r was shown by Stokes (1851) to produce a drag force $F = 6\pi\eta rv$, where η is a constant characteristic of the fluid, called its *viscosity*. Later Hadamard (1911) showed that for a spherical bubble of gas moving slowly through a liquid the drag should be only about two-thirds as large as that for a solid sphere, because the mobile molecules of gas effectively lubricate the boundary surface [2]. We will assume that the beer bubbles are small enough that they remain spherical as they grow and rise, and we will use Hadamard's formula for the drag. This completes our discussion of the physical basis for our model. More details about the actual behavior of bubbles in beer, including experimental data, can be found in [1].

The Mathematical Model

Let $x(t)$ denote the depth at time t of a CO_2 bubble in a glass of beer, with the surface taken to be $x = 0$, and the bottom of the glass at some negative value $x = x_0$, so that $x_0 \leq x(t) \leq 0$. Our model will have five parameters: the depth x_0 , the radius r_0 of the bubbles as they break free from a nucleation site on the bottom, the atmospheric pressure P and beer temperature T , and finally a constant K representing the rate at which carbon dioxide passes from the beer into the bubbles, per unit area of bubble surface. (The beer is kept under pressure until the glass is poured, so that a large amount of CO_2 is initially dissolved in the beer. The value of K gradually decreases as the beer goes flat, i.e., as its CO_2 partial pressure decreases.)

We first develop a differential equation for the amount of CO_2 in a bubble at depth $x(t)$. Let $n(t)$ denote the number of moles of CO_2 in the bubble at time t . The rate at which the gas enters the bubble is proportional to the bubble's surface area: $n'(t) = KA(t)$, and since the bubble is assumed to remain spherical, $A(t) = 4\pi r(t)^2$. If $V(t)$ denotes the volume of the bubble, then $V(t) = \frac{4}{3}\pi r(t)^3$, so $r(t) = [3/(4\pi)V(t)]^{1/3}$. Thus $n'(t) = 4\pi K[3/(4\pi)V(t)]^{2/3}$. By the ideal gas equation, $V(t) = [n(t)RT]/P(t)$. The pressure $P(t)$ in the bubble is the sum of the (constant) atmospheric pressure P and the fluid pressure of the beer on the bubble at depth $x(t)$. This fluid pressure, in turn, equals the weight of a column of beer of height $|x(t)|$ with unit cross-sectional area, or equivalently the weight density of the beer times the depth: $-g\rho_{\text{beer}}x(t)$, where g is the acceleration due to gravity and ρ_{beer} is the mass density of beer. Hence $P(t) = P - g\rho_{\text{beer}}x(t)$, which we substitute to get our first differential equation:

$$n'(t) = 4\pi K \left(\frac{3n(t)RT}{4\pi [P - g\rho_{\text{beer}}x(t)]} \right)^{2/3} \quad (1)$$

Now we turn to the equation of motion of the bubble: Newton's law, $m(t)x''(t) = F(t)$, where $m(t)$ is the mass of the bubble and $F(t)$ is the total force acting on it at time t . There are three vertical forces acting on the bubble as it rises: the buoyant force acting upward, i.e., in the positive direction on the x -axis, and the gravitational force and fluid drag acting downward. Archimedes' principle states that the buoyant force is equal to the weight of the beer displaced by the bubble: $g\rho_{\text{beer}}V(t)$. The gravitational force is just the weight of the bubble: $m(t)g = g\rho_{\text{CO}_2}(t)V(t)$. (The gas density $\rho_{\text{CO}_2}(t)$ varies with depth, while the beer density is essentially constant.) Substituting $m(t)/\rho_{\text{CO}_2}(t)$ for $V(t)$ in the expression for the buoyant force gives an expression that can be combined with the gravitational force on the bubble:

$$F_{\text{buoy}} + F_{\text{grav}} = gm(t) \left(\frac{\rho_{\text{beer}}}{\rho_{\text{CO}_2}(t)} - 1 \right).$$

Adding the (downward) drag force $-4\pi\eta r(t)x'(t)$ and dividing both sides of the equation of motion by the mass of the bubble then gives

$$x''(t) = g \left(\frac{\rho_{\text{beer}}}{\rho_{\text{CO}_2}(t)} - 1 \right) - \frac{4\pi\eta r(t)x'(t)}{m(t)}.$$

This is almost the differential equation desired, but we want the only variables on the right side to be the functions $n(t)$, $x(t)$, and $x'(t)$.

Now $\rho_{\text{CO}_2}(t) = m(t)/V(t) = m_{\text{CO}_2}n(t)/V(t)$, where m_{CO_2} is the mass per mole of carbon dioxide, a constant characteristic of this gas. By the ideal gas equation, $n(t)/V(t) = P(t)/(RT)$, so $\rho_{\text{CO}_2}(t) = m_{\text{CO}_2}[P - g\rho_{\text{beer}}x(t)]/(RT)$. By substituting this and replacing $m(t)$ by $m_{\text{CO}_2}n(t)$, and using the expression $r(t) = \{[3n(t)RT]/[4\pi P(t)]\}^{1/3}$ derived earlier, we then get our second differential equation:

$$x''(t) = g \left(\frac{\rho_{\text{beer}}RT}{m_{\text{CO}_2}[P - g\rho_{\text{beer}}x(t)]} - 1 \right) - \frac{4\pi\eta x'(t)}{m_{\text{CO}_2}n(t)} \left(\frac{3n(t)RT}{4\pi[P - g\rho_{\text{beer}}x(t)]} \right)^{1/3}. \quad (2)$$

We can reduce the system of differential equations (1), (2) by introducing the velocity of the bubbles as a new variable. The resulting system

$$n'(t) = 4\pi K \left(\frac{3n(t)RT}{4\pi[P - g\rho_{\text{beer}}x(t)]} \right)^{2/3}$$

$$x'(t) = y(t) \quad (3)$$

$$y'(t) = g \left(\frac{\rho_{\text{beer}}RT}{m_{\text{CO}_2}[P - g\rho_{\text{beer}}x(t)]} - 1 \right) - \frac{4\pi\eta y(t)}{m_{\text{CO}_2}n(t)} \left(\frac{3n(t)RT}{4\pi[P - g\rho_{\text{beer}}x(t)]} \right)^{1/3}$$

can be solved numerically, given appropriate initial conditions, to find the motion of a rising bubble.

Physical Constants and Initial Conditions

It is a useful task for students to track down the values of the physical constants that occur in these equations and express them in a consistent system of units. Using SI units, based on the meter for length, kilogram for mass, and second for time, we find that $g = 9.807 \text{ [m} \cdot \text{s}^{-1}]$, a typical atmospheric pressure is $P = 1.013 \times 10^5 \text{ [N} \cdot \text{m}^{-2}]$, the universal gas constant is $R = 8.3145 \text{ [N} \cdot \text{m}/(\text{mole} \cdot \text{K})]$, the mass per mole of CO_2 is $m_{\text{CO}_2} = 4.401 \times 10^{-2} \text{ [kg/mole]}$, and the density of a typical beer is about $\rho_{\text{beer}} = 1.010 \times 10^3 \text{ [kg} \cdot \text{m}^{-3}]$. Finding the viscosity of beer is more difficult, but [1] gives a measured value at 8°C of $\eta = 1.3 \pm 0.05 \times 10^{-3} \text{ [N} \cdot \text{s} \cdot \text{m}^{-2}]$, which is close to the published viscosity of water or ethyl alcohol at 10°C .

Finally, we have the constant K that measures the freshness of the beer, i.e., the rate at which CO_2 passes from the beer into the bubbles, per unit area of bubble surface. Estimating this value experimentally might be possible, but we will treat it as a “fudge factor,” choosing its value to make our numerically computed results conform to the experimental observation that the radius of bubbles in a tall glass of beer approximately doubles as they float to the surface.

Experiments [1] using a glass of beer filled to a depth of 15.6 cm (so $x(0) = x_0 = -0.156 \text{ [m]}$) with the beer temperature about 8°C (so $T = 281 \text{ [}^\circ\text{K}]$) found that the bubbles break free from the nucleation sites in the bottom of the glass when their radius is about 0.17 mm (so $r_0 = 1.7 \times 10^{-4} \text{ [m]}$). Using the ideal gas equation $n(t) = [P(t)V(t)]/(RT)$ once more, with $P(0) = P - g\rho_{\text{beer}}x(0)$ and $V(0) = \frac{4}{3}\pi r_0^3$,

yields the initial number of moles of CO₂ in the bubble:

$$n(0) = \frac{4\pi r_0^3 [P - g\rho_{\text{beer}}x(0)]}{3RT} \approx 10^{-10}.$$

We assume the bubbles break free with zero initial velocity: $y(0) = 0$.

Virtual Beer

Now the moment of truth: When we turn over to a computer the system (3), with the initial conditions just discussed, using a program for numerically approximating the solution, how does the behavior of the bubbles in our “virtual beer” compare with the experimental measurements [1] of the real thing? As mentioned above, some tinkering with values of the CO₂ diffusion rate coefficient K is required, but we find that $K = 7.5 \times 10^{-3}$ [moles · m⁻² · s⁻¹] produces the observed doubling of the bubble radius during the trip to the surface, using the experimentally measured value for the viscosity of beer and Hadamard’s formula for the drag force on the rising bubbles. However, we find that the bubbles in our virtual beer reach the surface in less than one second! If we decrease the value of K , slowing the rate of growth of the bubbles and hence retarding their increase in buoyancy, we can make them take the required 3.8 seconds to ascend—but then we find that their radius is nearly constant throughout the trip. There is no value of K that will produce the desired doubling in bubble radius and also a rise time of about 3.8 seconds. Our plausible model produces virtual beer that is quite unlike the real thing!

The flaw in our model appears to be that the drag force is neither Hadamard’s $-4\pi\eta r(t)x'(t)$ nor Stokes’s $-6\pi\eta r(t)x'(t)$. Apparently the bubbles rise too rapidly to satisfy the assumptions of “creeping flow” on which these formulas depend, or possibly some other effect we have ignored has a significant bearing on the drag. However all is not lost—we may yet gain some insight into the motion of the bubbles by assuming that the drag force is proportional to the radius and speed of the bubbles, but no longer insisting that the coefficient of proportionality be a known multiple of the viscosity of beer. Thus we may suppose the drag force is of the form $F_{\text{drag}}(t) = -d r(t)x'(t)$, where the coefficient d is, like K , a “fudge factor” that we can adjust to make the bubbles rise in the desired 3.8 seconds while doubling in size. When this is done, we find that the choice $K = 2 \times 10^{-3}$ [moles · m⁻² · s⁻¹] and $d = 0.068$ [N · s · m⁻²] gives acceptable results, shown in Table 1. However, scrutiny of the table shows that the bubbles in our virtual beer

Table 1

t	Computed 100 $x(t)$	Measured 100 $x(t)$	Computed $r(t)/r_0$
0	-15.6	-15.6	1
0.54	-14.5	-14.4	1.15
1.08	-13.1	-12.2	1.29
1.62	-11.3	-10.4	1.44
2.16	-9.2	-8.6	1.58
2.70	-6.5	-6.0	1.73
3.24	-3.4	-3.2	1.88
3.78	0.2	0	2.03

Table 2

t	Computed $100x(t)$	Measured $100x(t)$	Computed $r(t)/r_0$
0	-15.6	-15.6	1
0.54	-14.0	-14.4	1.15
1.08	-12.2	-12.2	1.29
1.62	-10.3	-10.4	1.44
2.16	-8.0	-8.6	1.58
2.70	-5.6	-6.0	1.73
3.24	-3.0	-3.2	1.88
3.78	-0.1	0	2.03

begin by rising too slowly (falling almost 1 cm behind), then accelerate enough to reach the surface in the same time as bubbles in genuine beer.

Could better results be obtained by continuing to assume that the drag is proportional to the speed of the bubbles, but is proportional to their cross-sectional area rather than their radius? That is, assume $F_{\text{drag}}(t) = -dr(t)^2x'(t)$ for some constant d . All that is required is to change the exponent in the equation for $y'(t)$ from $\frac{1}{3}$ to $\frac{2}{3}$, and to experimentally determine appropriate values of the constants K and d . We find that the same value of K , together with $d = 260$ [$\text{N} \cdot \text{s} \cdot \text{m}^{-3}$], gives bubbles that double in size while rising to the top in about 3.8 seconds. Moreover, the bubbles in our virtual brew now ascend at about the same rate as those in real beer; see Table 2. The uncertainty in the measured values is of the same order of magnitude as the deviations from our computed values, so further attempts to refine our model to fit the experimental data would be pointless.

This example illustrates the importance of comparing the results of models with experimental data. Our quite plausible model, based on well-known physical principles, gave a poor performance. This is not uncommon in fluid dynamics, a subject fraught with complications and paradoxes. By simplifying the model—abandoning the hope of expressing the drag in terms of fundamental constants, like viscosity and density, that characterize the fluid properties of beer—we obtained reasonable agreement between bubble behavior in virtual beer and the real thing.

We've gained some insight into the phenomenon of bubble formation and motion, but there remain plenty of mysteries to contemplate when next we gaze into a full pilsener glass. Working through this analysis may have left you with a parched palate—perhaps more experimental investigation is called for . . . Cheers!

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