THE AMATEUR SCIENTIST

Drops of liquid can be made to float on the liquid. What enables them to do so?

by Jearl Walker

Twice in this department the late C. L. Stong presented experiments having to do with the curious phenomenon in which water drops glide across a water surface for several seconds before sinking into it. You may have seen this happening in an automatic coffee maker when water drips from the filter into the glass container.

In the first of Stong's discussions (August, 1973) Gerard Schol described an apparatus for studying the drops and argued that the support was probably due to an electrical repulsion between the bottom of a floating drop and the bulk liquid just below it. In the second discussion (April, 1974) Kenneth C. D. Hickman experimented with something a bit different: water drops called boules that floated on slightly superheated water. For me the boules are more easily understood than the drops described by Schol because the superheated fluid has a large rate of evaporation and the resulting vapor layer below the drop supports it. A similar support mechanism holds water drops just above a hot plate in the Leidenfrost phenomenon I discussed in this department last August.

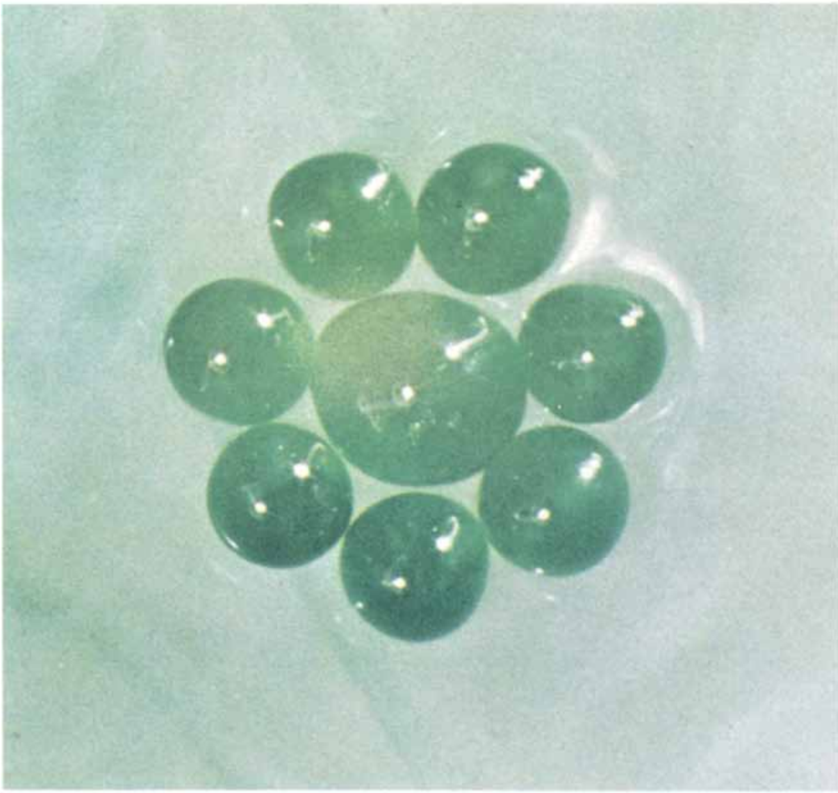
The phenomenon of water drops that float on water that is at room temperature has attracted attention for a long time. John Tyndall examined such drops as early as 1885, and in 1881 Osborne Reynolds wrote "On the Floating of Drops on the Surface of Water Depending Only on the Purity of the Surface." Although Reynolds did not specify the support mechanism, he probably thought it was due to surface tension. His discussion indicated that floating drops are relatively rare because impurities on a typical water surface somehow destroy the flotation mechanism.

Although the nature of the support has been discussed for almost a century, I do not think the final word has been written yet, largely because of a clever experiment that has recently been described to me by James A. Raymond of the Alaska Department of Fish and Game. Raymond points out that the lifetime of the floating drops can be increased from about a second to several seconds, perhaps tens of seconds, by adding detergent to the water. That much has been well known. The remarkable thing Raymond has discovered is that the drops can be made to last for several minutes by vibrating the container in such a way that standing waves are set up in the surface of the water. In fact, some of Raymond's drops lasted as much as 18 minutes. He suggested using a household appliance such as an electric hair clipper to vibrate the side of a cake pan containing the solution of water and liquid detergent (two teaspoons per quart of water). To achieve more consistent results he put a one-liter plastic beaker of the solution on a slightly unbalanced tabletop centrifuge. Occasionally he obtained drops almost two centimeters in diameter by allowing several smaller drops to combine or by building them up slowly with a syringe filled with the solution.

Other workers have reported that the drops often refuse to perform individually but that if a steady stream of drops is played on the surface of the bulk liquid, the drops eventually begin to float. The common explanation of the survival of the later drops is that the early drops sweep the surface of the bulk liquid clean of the impurities that somehow eliminate the support mechanism. Raymond points out that part of the success of the stream of drops may be that the earlier drops make the bulk surface vibrate slightly, thereby enabling the later drops to float for a while.

Raymond found two other interesting things. His drops were repelled by air bubbles on the surface but were attracted by one another. The repulsion and attraction appear to have to do with the shape of the water surface near the air bubbles and the drops. The surface curves up on the bubbles, and a drop will not climb uphill. The surface curves down into a dimple around each drop, so that two adjacent drops can easily flow toward each other. When they meet, they may remain as two drops, suddenly coalesce to form a single drop or disappear.

In repeating Raymond's experiment I replaced the household vibrator with a six-inch loudspeaker and an audio oscillator, both of which you can buy from



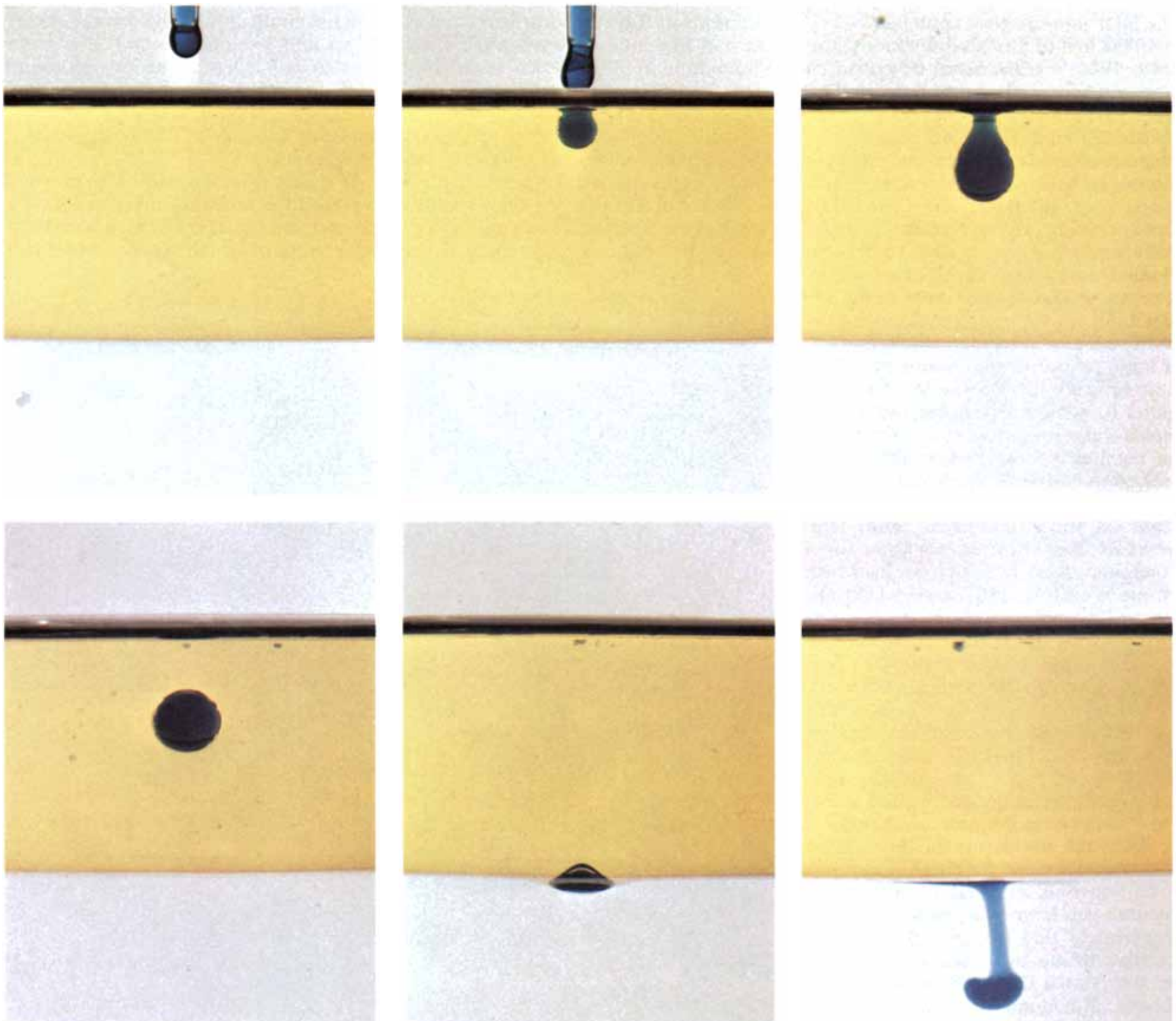
Flowerlike pattern of floating drops of dyed water a dealer in electronic equipment. The speaker had no front covering and was placed faceup on a table. Over it I put a curved watch glass large enough to cover it. The curved glass or plastic face of a clock will serve, or you can buy a chemical watch glass from a chemical-supply house. The advantage of my setup was that I could control the amplitude and frequency of the vibration. In particular I could easily tune the vibrations in and out of resonance for the speaker-air-glass-liquid system and also see how the lifetime of the drops depended on the vibrational amplitude.

I mixed about 12 milliliters of Ivory liquid detergent in 100 milliliters of tap water, poured some of the mixture into the watch glass and filled a syringe with the solution. (You could use an eyedropper.) When I squirted drops onto the water, the results were just as startling as Raymond must have found them. When the audio oscillator was tuned to resonantly oscillate the water (even gently) so as to cause vibrational standing waves to form on the surface, the drops lasted for several minutes. With my system this result appeared at oscillation frequencies between 10 and 150 hertz. (I could not go lower than 10 hertz on my audio oscillator.)

When I tuned the oscillator out of resonance so that the standing waves disappeared (one can do so either by tuning to a higher frequency or by decreasing the amplitude of the oscillator), the drops coalesced into the bulk liquid within a few seconds. Only with the vibrational waves present would the drops float for longer than 10 seconds or so. Before receiving Raymond's letter I had become accustomed to having the drops last for such a brief time that I had trouble examining them properly, and now I had drops lasting so long that I could go out for a cup of coffee while they persisted.

Most of the floating drops were from a millimeter to a few millimeters in diameter, about the size of the wavelength of the surface waves on the water when the oscillator was at 50 hertz. By making several small drops coalesce or by continuously discharging fluid from the syringe into a single drop I built up larger drops that significantly dimpled the water surface and were larger than the wavelength of the surface waves. If adjacent drops did not coalesce to form a single drop, they formed rafts of floating drops. I had rafts two or three centimeters across, each consisting of about a dozen drops. With some care I could make a pretty design consisting of one large central drop surrounded by a ring of smaller drops. When I later began to use food coloring in the drops, I was able to make red and blue rafts of this flowerlike design.

As other investigators have found, the drops did not always behave. No one has understood their fickle nature, but presumably their refusal to form is partly due to variations in the local electric field. For example, an experimenter



Motions of a drop of dyed vinegar put on a layer of corn oil above a layer of vinegar moving past the apparatus can alter the electric field near the drops and cause them to merge into the bulk liquid. Surface impurities are also important, because dust on the surface prevents the drops from floating. I tried blowing a light layer of lycopodium powder, an organic hydrophobic powder available from chemical supply houses such as Fisher Scientific Company (26401 Miles Ave., Cleveland, Ohio 44128) for about $7 for four ounces, on the surface and immediately lost my ability to generate floating drops.

The generation of floating drops also appeared to depend on the height from which the drop fell from my syringe. If I carefully allowed a drop to form on the needle and fall of its own accord, it would float if the distance of fall was within a certain range. Well above that range drops might still float but only if the drop splashed into the bulk liquid hard enough for the spray thrown upward to produce floating drops.

Most of the drops, particularly the larger ones, seemed to rest quietly in the nodes (the places of minimum surface vibration) of the standing waves. This positioning was difficult to verify, however, and the larger drops caused such a dimpling of the surface that surely any standing-wave pattern on the surface was distorted in that area. Some of the smaller drops continuously hopped up and down in the pattern with the same type of frenzied vibration I had seen in the Leidenfrost effect.

One explanation of the support mechanism is that water molecules on a water surface orient themselves so that the surface is electrically negative. Hence the bottom of a drop, being negative, is repelled by the surface of the bulk water, which is also negative. The only proof of this repulsion mechanism I have seen is that the presence of an external electric field near the drop destroys the floating. The same thing might happen, however, even if the support mechanism were nonelectric, because the external electric field would destroy it.

Assume that a negatively charged rod is placed above a floating drop. Regardless of whether the drop is slightly charged or is neutral, the electric field of the rod polarizes the drop so that its top (nearer the rod) is positive and its bottom (farther from the rod) is negative. Just below the drop the surface of the bulk liquid becomes positive. Since that surface and the oppositely charged bottom of the drop are so close, the drop is pulled into the liquid. Thus an external electric field can make the drop coalesce into the bulk liquid even if the drop is not normally supported electrically. Electric fields are often employed to make airborne drops coalesce in a similar fashion in order to precipitate out undesired mists.

Another (and more widely accepted)

explanation is that the support mechanism is the thin layer of air that is trapped below a drop just as it reaches the surface of the bulk liquid. The air forms a layer from 100 to 1,000 nanometers thick and may be at a pressure high enough to dimple the bottom side of the drop in the same way that the surface of the bulk liquid is dimpled. The lifetime of the drop is determined by the rate at which this air leaks out through the even narrower gap that rings the dimpled area. Eventually the air layer thins enough (to less than 50 nanometers) for the weight of the drop to rupture the layer. Then the drop either coalesces into the bulk liquid or re-forms into a smaller floating drop.

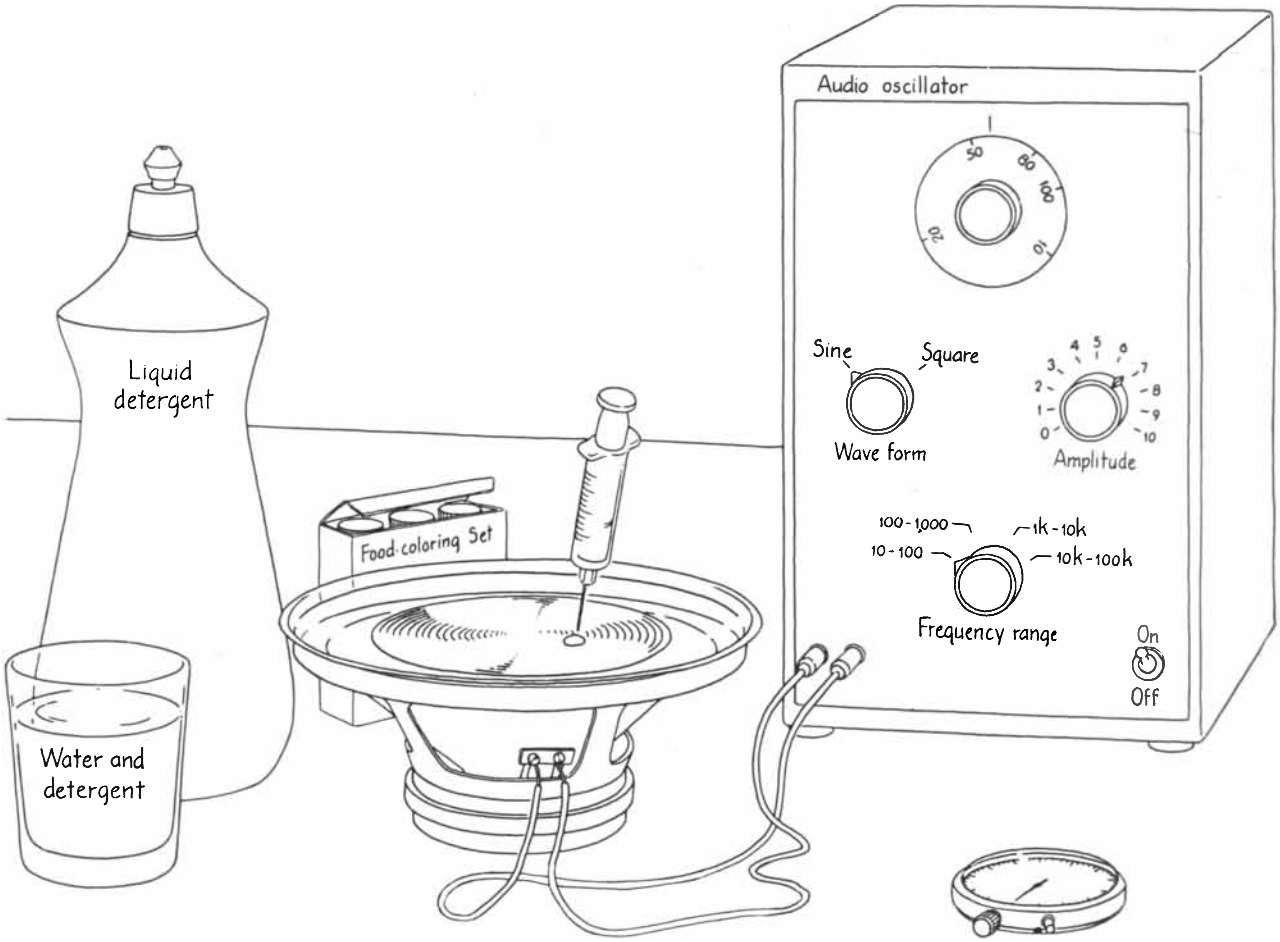
The leakage rate depends on three factors: the possible imbalance of surface tensions on the bulk surface, the surface viscosities of the bulk liquid and the drop, and the viscosity of the air trapped below the drop. As air leaks out it attempts to drag the top layer of the bulk liquid along with it. If the liquid has a high surface viscosity, the flow of both the liquid and the air is retarded, and the drop lasts a relatively long time. The addition of detergent to the water increases the floating time for this reason. Although the detergent lowers the surface tension of the water, it increases the surface viscosity. If the air is replaced with a more viscous gas such as carbon dioxide or with a viscous liquid, the leakage rate would also be decreased and the drop lifetimes increased.

The uniformity of surface tension over the local surface of the bulk liquid is also important. Suppose the surface tension just below a drop were lowered by the vapor emitted by the drop. Then the stronger surface tension just outside the contaminated area will pull the bulk liquid radially outward, dragging the trapped air along with it, thereby decreasing the drop's lifetime. Such motion across a liquid surface because of nonuniform surface tensions is called the Marangoni effect after Carlo G. M. Marangoni, who studied it in the latter half of the 19th century. With a water drop the lifetime of from three to 10 seconds depends primarily on the viscosity of the air and the surface viscosity of the solution of water and detergent.

The concept that air is trapped below the drop helps to explain why my drops floated if the height of fall was within a certain range. If I casually released a drop just above the water surface, the drop reached the surface with a relatively low velocity and apparently did not trap air. A greater height gave a greater velocity and trapped enough air to support the drop. If the height of fall was even larger, the splash (either the crown ringing the impact point or the central vertical jet following the relaxing crown) could produce drops that would float on the water.

The model also explains the absence of floating drops on dusty or dirty water. Any dust particle or hair on the surface would puncture the air layer and cause the drop to merge with the bulk liquid.

Even if one accepts this model for the support mechanism, it is still necessary to explain why the vibration of the bulk liquid increases the lifetime of a drop. Raymond suggested that the vibrations might somehow pump air under the drop, so that it continues to be supported. This idea was appealing to me because it was in line with the generally accepted hypothesis that trapped air is the support mechanism. The pumping could possibly come from circulation patterns in the bulk surface that would drag air under the drop. Imagine a small drop sitting at the node of a standing-wave pattern. As the fluid areas to the left and right of it oscillate out of phase with each other, there could be a periodic exchange of the bulk liquid between



Arrangements for making a drop-bearing surface oscillate left and right under the drop, dragging air below the drop in the process. Even without surface circulation the combined oscillations of the surface and the drop might somehow periodically trap more air under the drop.

Although air may be pumped under the drops in this way, the model presents several problems. First, I do not quite see how the combined oscillations of the surface and the drop can force more air under the drop while the weight of the drop is trying to squeeze air out of that area. Second, the rafts of drops I have described are difficult to explain unless one argues that the air trapped below the central drops is so far from the perimeter of a raft that it does not leak out as readily and therefore does not need to be replaced.

A third problem is more troublesome. Try as I might, I could detect no circulation of water near an individual floating drop. To trace circulation I put a small amount of dye in the bulk liquid and arranged for a thin filament of the dye to be near a drop. I worked with two types of dye: a red fuchsin (from chemical supply houses) and a common blue or red food coloring. In small quantities neither dye appeared to alter the support mechanism of the drops by radically changing the surface tension or the viscosity of the bulk liquid. I could move a drop near a dye filament by placing the needle of my syringe near the drop. Because the liquid curved upward onto the needle the drop moved away. When a drop reached a dye filament, any circulation below the drop could be expected to carry part of the filament with it. I seldom saw such an effect. If there is circulation below the drop, it is surprisingly slow, even imperceptibly slow. I did find circulation patterns when two or more drops were floating side by side; here the vibrations of each drop would alter the vibrations of the others. This circulation could possibly add air under the drops.

I also checked to see if the drop had an internal circulation that could pump air below the drop. I first built up a large floating drop by making several smaller drops coalesce. Then I added a small colored drop. After several tries I made the small dyed drop coalesce with the larger transparent drop, and this addition of dye to the large drop enabled me to search for internal circulation patterns. In particular I thought the drop might develop a downward flow on its outside and an upward flow in its center, thus dragging air under itself. The dye tracer revealed no such internal pattern. In fact, the dye spread itself through the drop rather slowly, and any immediate motion of the dye appeared to be due to the spinning of the drop as a whole resulting from the disturbance of the coalescence.

Why, then, do drops placed on a vibrating liquid surface last so much longer? Other experiments have ruled out an electrical repulsion as the main support mechanism, and I do not see how such a force would be enhanced by vibration anyway. As appealing as circulation patterns pumping air below a drop are to me, I cannot find any readily apparent circulation. The fact remains that the drops do last significantly longer on a vibrating surface.

My best clue came from examining the floating drops under a strobe light set near the frequency of oscillation, so that the flashing light effectively slowed the vibration of the drops. I found two types of vibration among the drops. The very small drops were oscillated so much by the vibrating surface that they hopped up into the air each time the surface pushed upward. Presumably these drops retrapped air on reaching the bulk surface again, thereby delaying their coalescence into the bulk liquid until some chance mishap destroyed them.

A larger drop, on the other hand, did not leave the surface, and its center of mass did not appear to move much vertically. The drop oscillated by periodically varying its shape from relatively tall and thin to relatively short and fat. From overhead this variation in size was symmetric around the drop. Surrounding the drop were concentric circles of surface waves apparently generated by the drop's vibrations.

I think that whenever the bulk liquid directly under a drop pushed upward on the air layer, the bottom of the drop was in turn pushed upward, forcing the drop to spread outward. Since the drop was oscillated at or near resonance by the bulk liquid, a phase difference of between 0 and 90 degrees between the two motions should arise. In other words, the drop could lag behind the bulk liquid by as much as a fourth of the oscillation period. The radial spread of the drop pushed in turn (by way of the air layer) on the rim of the dimple, sending off a crest in the surface waves. Whenever the bulk liquid descended below the drop, the drop became thinner and expanded vertically as the rim of the dimple pushed radially inward.

This pushing along the rim should on the average decrease the tiny gap through which the air must eventually escape if the drop is to coalesce with the bulk liquid. The rate of escape depends on the cube of the gap's width, which means that if the gap is diminished somewhat, the escape time might be significantly longer. Suppose the gap is narrowed from a typical 200 nanometers in a calm situation to an average 50 nanometers in the vibrating situation, that is, decreased fourfold. The escape time and hence the drop lifetime would increase by 4^3, or 64 times. If the lifetime is typically 10 seconds on a calm surface, it would be almost 11 minutes on the vibrating surface. Thus a drop evidently lasts longer because the vibrations narrow the escape route of the air supporting the drop.

When I placed two drops side by side, each one perturbed the oscillations of the other and distorted the component of radial expansion in their vibrations. From overhead I saw each drop change from being oblong perpendicular to a line through the centers of the drops to being somewhat oblong parallel to the line. The drops were always in phase in these changes. Using a dye tracer I found that bulk liquid was pulled in under the drops from both sides along the line through their centers and then was pushed outward between the drops perpendicular to that line.

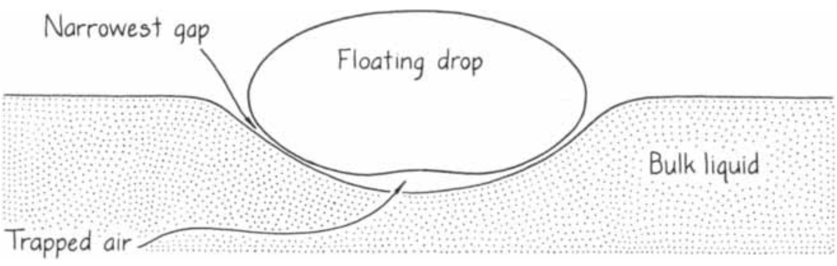
Some of my data for the lifetime of drops at 50 hertz are plotted in the illustration on page 158 as a function of the uncalibrated amplitude settings on the audio oscillator. The drops were all approximately the same size (a few millimeters in diameter) and were allowed to fall approximately the same distance. They were not allowed to coalesce with other drops. (I had the impression that coalescence lengthened the lifetime of the drops, but I did not verify it.) I have no basis for assuming that the relation between the amplitude setting and the amplitude of the vibrations in the water in my watch glass is linear; it is probably quite complicated. Nevertheless, you can see two interesting features in these data. With little or no amplitude of oscillation the drops lasted a fairly short time. In the midrange they lasted the longest. At greater amplitudes the lifetimes decreased, presumably because the oscillations in the bulk liquid were so violent that a drop was thrown around and lost its air support. The second interesting feature is that even when some drops lasted a long time (my record was about 10 minutes), other drops at the same amplitude setting and under seemingly identical circumstances lasted only a short time.

I tried isolating a floating drop by various means: drawing rafts of air bubbles around it, lowering a ring around it or dipping a loop of wire into the bulk liquid and then pulling the wire upward to place a soap bubble over the floating drop. As long as the water around the drop continued to vibrate, even gently, the drop could last a long time.

You might wonder why touching drops do not always immediately coalesce. I believe a layer of trapped air must lie between them just as one lies below them. When two drops come together, they essentially fall into each other's dimple and hence gain some horizontal speed. If that speed is large enough, air could be trapped in the touching and could take some time to leak out. Eventually the air layer is thin enough for the drops to coalesce to form a single drop. Alternatively, the disturbance ruptures the support layers and the drops coalesce into the bulk liquid. How they coalesce into each other is important in studies of fogs and mists where airborne droplets touch and possibly coalesce to form larger drops.

The fluid supporting a drop does not have to be air or even a gas. All that is needed is a drop that falls through another fluid in which it will not mix and then encounters a bulk layer of its own kind. As an example I poured a layer of vinegar into a beaker and then added a layer of corn oil. Each layer was at least two centimeters thick. With my syringe I squirted small amounts of vinegar in a single area of the surface of the corn oil, gradually building up a drop that hung from the oil-air surface. Eventually the drop was heavy enough to break from the surface and fall to the bulk vinegar layer. At first the fall made the drop go faster, but as it approached the vinegar layer it noticeably slowed down because the corn oil between it and the oil-vinegar interface had to be squeezed out of the way. When the drop reached the interface, some oil was still trapped below the drop, which therefore sat on the interface with the same dimple feature characteristic of the water drops. After about a minute the drop broke into the vinegar layer, apparently because the layer of corn oil under it had become sufficiently thin. I dyed the vinegar drops so that I could more easily watch this rupture and the resulting flow of new vinegar into the vinegar layer. The sight of a blue or red drop sitting in the yellow corn oil waiting for the thin layer of oil to get out of the way struck me as beautiful.

Does vibrating the container of vinegar and corn oil prolong the lifetime of the vinegar drops sitting on the interface of the two liquids? The answer is yes. When I placed the container on my watch glass and resonantly vibrated the assembly as before, the drop lifetimes



Trapped-air mechanism for making a drop float

SCIENCE/SCOPE

The Pioneer Venus mission consists of two spacecraft built by Hughes for NASA's Ames Research Center. Orbiter will circle Venus for at least one Venusian year (225 earth days), studying the atmosphere, winds, magnetic and gravitational fields. Multiprobe will send four probes toward the surface to measure clouds, energy and wind. Altogether, 30 instruments will be flown and supported by 115 scientific investigators, co-investigators and team members. Since Venus' major weather patterns are global in nature, the data obtained should help scientists learn more about the forces that drive the weather on earth.

Printed repair manuals may soon be replaced by an electronic display, part of the Technician's Maintenance Information System (TMIS) developed by Hughes. It can direct the repair of complex equipment simply by asking the repairman to describe his problem. It comes in two portable packages: a video display with electronic keyboard; and a mass memory device using floppy disks, plus a microprocessor.

A technician simply selects the appropriate disk, loads it into the system and types in the problem. In less than two seconds, the display screen provides a series of questions. After he provides the answers, the system pinpoints the failure, the part needing replacement, shows its location, and tells how to replace it. With this method, many repairmen will no longer require extensive technical training or cumbersome stacks of data. By cutting troubleshooting and repair time to a small fraction of present needs, costs can be reduced drastically.

A new kind of instrument will help meteorologists gauge more accurately the direction and speed of winds at all altitudes -- and thus improve long-range weather forecasting -- when the first of three Hughes-built weather statellites is launched from the Space Shuttle in the early 1980's. Intended for use along with similar spacecraft from Europe, Japan and the Soviet Union, the Geostationary Operational Environmental Satellites (GOES-D, E and F) are U.S. entries in an international weather-watch program. NASA manages the construction and launch of GOES for the National Oceanic and Atmospheric Admin., which generates the satellite system.

Heart of the new satellites will be a Visible Infrared Spin-Scan Radiometer Atmospheric Sounder (VAS), built by Hughes' Santa Barbara Research Center, that will produce day and night pictures of the Earth's cloud cover, as well as determining the three-dimensional structure of atmospheric temperature and humidity.

Hughes Industrial Products Division, located near San Diego, California, is seeking Electronics Engineers/Technicians and Physicists to work on: Ultrasonic Scan Converters (Medical Applications); Infrared Detectors (Police and Firemen); Microelectronic Welders (Industry); Flexible Automatic Circuit Testers (Airlines, Phone Companies); Cathode Ray Tubes (Airlines); Laser Cutters (Apparel Industry). For immediate consideration, please send your resume to: Jim Burley, Hughes Aircraft Company, Industrial Products Div., 6155 El Camino Real, Carlsbad, CA 92008.

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increased from about one minute to between 2.5 and three minutes.

When an air bubble rises through a fluid and impinges on a flat object, such as the bottom of a beaker immersed in the fluid, the fluid requires some time to get out of the way, just as the oil did with my vinegar drops. The bubble first reaches the flat barrier with a thin layer remaining between the air and the barrier. At a rate depending on the viscosity of the fluid the layer flows out of the way, finally becoming so thin that the bubble breaks and the air touches the barrier directly.

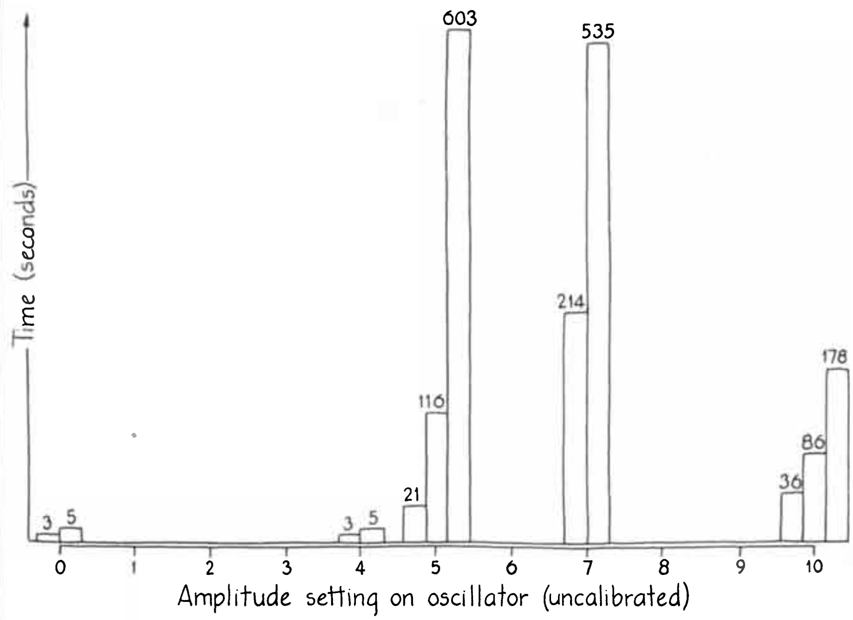
A lot more work could be done on floating drops. With air as the support layer you could try floating drops of fluids other than water. I was able to float drops of rubbing alcohol on a layer of rubbing alcohol. You might try oils, both in the floating-drop and rising-bubble experiments. Does the lengthening of drop lifetimes by vibration work in deeper water? I don't know. You might want to find out. Does a long lifetime for a drop require vibrational waves that are about the size of the drop? Will drops float for several minutes if the vibrational frequency is well above 150 hertz or below 10 hertz?

You also might want to work with gases other than air or with supporting liquids other than corn oil. Does vibration always help? In the water-drop experiment you could attempt to correlate the concentration of the detergent with the lifetimes of drops. In particular you might be able to find a leveling off of the lifetimes after a certain concentration, which would imply a leveling off of the change in surface viscosity due to the detergent. If the vibrational pattern in a water-drop experiment is quite steady, will the drops float for hours, or is the upper limit about 18 minutes? If the duration is unlimited, my explanation of how the vibrations lengthen the time is wrong.

While you are playing with water and occasionally reflecting on surface tension you might want to repeat an old parlor trick. Fill a glass with clean water, sprinkle pepper over the surface and touch one side of the surface with a bar of soap. The pepper particles zip to the opposite side of the surface.

This motion across the surface is another example of the Marangoni effect. The soap film deposited on the surface immediately lowers the surface tension, and the area free of soap then contracts because of its greater surface tension. The pepper particles are merely caught up in the contraction and taken for a quick ride.

In another parlor trick small particles of camphor (available from chemical supply houses as *dl*-camphor) are placed on the surface of clean water. Because of the uneven rate at which the camphor dissolves around its perimeter, the particles dance to and fro in a merry jig. Suppose one particular corner of a particle dissolves first. The local surface tension is lowered and the particle is pulled by the greater surface tension on its other side. Then another corner dissolves, and again the particle is pulled on the opposite side. Finally enough camphor has dissolved for the surrounding surface tension to fall just below the value needed to pull additional molecules out of the particle, and the dance ends. Years ago children played with toy boats propelled by a bit of camphor or alcohol placed at the rear of the boat. Either substance lowered the local surface tension, causing the greater surface tension at the bow to pull the boat forward.



Floating times of water drops on a water-detergent surface