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Persisting Water Droplets on Water Surfaces†

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Abstract

Droplets of various liquids may float on the respective surfaces for extended periods of time prior to coalescence. We explored the features of delayed coalescence in highly purified water. Droplets several millimeters in diameter were released from a nozzle onto a water surface. Results showed that droplets had float times up to hundreds of milliseconds. When the droplets did coalesce, they did so in stepwise fashion, with periods of quiescence interspersed between periods of coalescence. Up to six steps were noted before the droplet finally vanished. Droplets were released in a series, which allowed the detection of unexpected abrupt float-time changes throughout the duration of the series. Factors such as electrostatic charge, droplet size, and sideways motion had considerable effect on droplet lifetime, as did reduction of pressure, which also diminished the number of steps needed for coalescence. On the basis of present observations and recent reports, a possible mechanism for noncoalescence is considered.

I. Introduction

When a droplet of liquid falls onto the surface of the same liquid, instant mixing is generally expected. However, even in everyday situations, small droplets can sometimes be observed to float on surfaces without instant mixing, for example, when droplets fall into sinks or during rainfall, when splashes create tiny droplets that may move swiftly across puddle surfaces. Despite such common experience as well as a number of relevant scientific studies, still, the concept of delayed coalescence remains counterintuitive.

A number of hypotheses have been proposed to explain the delayed coalescence. In 1900, Reynolds¹ proposed that droplets can reside on the liquid surface because a thin film of air becomes entrapped underneath the droplet. However, Mahajan² later reported that water did not form floating droplets at atmospheric pressure but that droplets could be more easily produced at higher altitudes where air pressure was lower, the opposite of what was expected from Reynolds's hypothesis. The positive effect of reduced air pressure was more recently confirmed in studies of oil-droplet lifetime.³ Because diminished air pressure should diminish the thickness of any air cushion, these latter observations have seemed difficult to reconcile with the early air-cushion hypothesis.

On the basis of experimental results obtained when bulk and droplet fluids are different, Hazlehurst and Neville⁴ proposed that delayed coalescence might originate from the fact that different liquids have different molecular structures, and thus some molecular

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Supporting Information Available: A movie demonstrating coalescence cascade of the water droplet. This material is available free of charge via the Internet at <http://pubs.acs.org>.

rearrangement must take place for coalescence to occur. Depending on the extent of difference, noncoalescence duration could be shorter or longer. The group was unable to observe delayed coalescence of water upon water. The water used in those experiments remains of unclear origin and purity. Whether distilled, deionized water was capable of producing floating droplets remained unclear.

In this study, an attempt was made to fill this gap. Experiments confirmed that under suitable conditions, pure, deionized water does form noncoalescing droplets. Several factors were identified to influence float duration and dynamics of coalescence. On the basis of the results and on recent data,⁵ we propose a hypothesis to explain the absence of instant coalescence.

II. Methods

The experimental apparatus is schematized in Figure 1. Distilled, deionized water (10 mL, type 1, HPLC grade, 18.2 M Ω), obtained from a standard water purification system (Diamond TII, Barnstead), was delivered onto a glass slide (W: 50 mm, L: 75 mm, H: 1 mm, Brain Research Laboratories, Newton, MA). This provided a water layer several millimeters thick on the receiving surface.

The glass slide with water was supported on an aluminum-walled platform with a light-diffusing glass as the top surface. An LED (Phillips Luxeon Star, LXHLME1D, Cyan) was housed inside the platform to illuminate the diffusing glass from beneath. This created uniform background illumination beneath the water for video recording. Light intensity was controlled via LabView software, which was coupled to a DAQ board (NI USB-6009) and a custom-built amplifier.

The droplets were generated by supplying water, obtained from the same source as above, from a syringe to a stainless steel nozzle located above the bulk water. The nozzle was housed in a stainless steel tube, which penetrated through the lid of the chamber through an airtight rubber gasket. The steel tube was connected to the syringe through a length of Tygon tubing. The flow of water to the nozzle was created by the syringe pump (YA-12, Yale Apparatus), which pushed on the syringe plunger at a constant rate. To regulate the height of the droplet above the water surface, the stainless steel tube was attached to a linear translator that allowed vertical movement of the tube and nozzle. The tip of the nozzle was first set to the level of the water surface and then raised to a position 5 mm above, as marked by the scale on the translator.

The entire apparatus was housed in a 1 cm thick transparent plastic vacuum chamber. The base of the chamber was made of aluminum, and the chamber was caulked to ensure against air leakage. Three openings in the chamber base allowed for connections to the vacuum pump, the air-pressure gauge, and a release valve.

For experiments with reduced air pressure, two methods were used for extracting air from the chamber. For the relatively higher pressures (100 to 30 kPa), the house vacuum was used; for the lower pressures (20 and 10 kPa), an oil-vacuum pump (Lammert 10301) was used. A pressure gauge (VWR Traceable, 0–690 kPa) was used for determining the pressure inside the chamber. The entire apparatus was grounded to reduce residual charge because previous experiments had indicated that static charges seriously impacted coalescence repeatability. (See below.)

To record events, a digital video camera (Edmund Optics, EO-0413 M MONO USB) was used at a frame rate of 200 frames per second. Recording commenced when the droplet began to detach from the nozzle and continued until after it had completely coalesced. We

analyzed the data by counting frames from the moment of impact onward. The number of frames times the frame rate gave the residence time.

For droplet counting, a laser and a photosensor were used. The photosensor was connected to a computer via the DAQ board. As the incipient droplet grew, it broke the path of the laser beam; once the photosensor voltage dropped below a predetermined threshold and subsequently returned to its original value upon droplet's detachment, the LabView program registered a droplet in a counter.

The water used in experiments was prepared by one of the two methods. In the first, water from the purification unit was collected in a beaker and immediately loaded into the supply syringe and dispensed onto the glass slide. This was considered to be "unequilibrated" water. In the other method, the water obtained from the purification unit was placed in a beaker and equilibrated for 1 h in a vacuum chamber at the pressure to be studied. Then, 10 mL of that water was placed on the glass slide and into the syringe. Each trial was conducted immediately after the end of the 1 h equilibration.

The glass slide was handled only by gloved hands (Cardinal Health Powder-free Latex Exam Gloves) and was first washed with Soft Scrub and rinsed thoroughly in tap water. Once the soap was fully removed, the glass slide was thoroughly rinsed in deionized water. The slide was then dried by an air jet. The glass was inspected for debris, and if any was found, then the process was repeated.

III. Results

1. Noncoalescence Phenomenon

Droplets of water were released from a nozzle situated 5 mm above the water surface. The droplets grew at the tip of the nozzle to ~3 mm in diameter and then detached into free fall. Some droplets coalesced immediately with the water beneath, but the majority did not.

An example of the latter is shown in the sequence of Figure 2. When the falling droplet first encountered the water surface, it broadened (0), then depressed the surface (12), and after a few minor oscillatory movements, finally came to a stop (40). The impact created a wave, which propagated away from the center point. No change was observed for the next 50 ms; the surface around the droplet remained still (92). Then, abruptly at 96 ms there was a dramatic change. A liquid connection formed between the droplet and the bulk in the shape of a cone-shaped skirt above the surface (96). The droplet seemed to expel some of its contents into the skirt beneath, while extending slightly upward. Meanwhile, the top portion of the skirt narrowed into a column (100) while the original extrusion on bulk surface turned progressively into a depression (96 to 104 ms). These movements generated a series of waves propagating away from the coalescence site.

Once the liquid connection had formed (as at 96 ms, above), one of the two scenarios followed. In the first scenario, complete coalescence was achieved. In the second and more dominant scenario, as illustrated above and described in detail next, coalescence took place in a series of steps.

2. Coalescence Cascade

In the cascade scenario, the original droplet coalesced only partially. The liquid column (Figure 2, 100 ms) elongated upward while thinning at the bottom to form a "bulb." The bulb is shown again in Figure 3 at 135 ms. Eventually, the column broke and retracted upward into the bulb, producing a new droplet suspended in the air. The new droplet, referred to as "secondary", was smaller than the original one, and sometimes, instead of one

droplet, there were two. This happened when the water column broke in two places simultaneously along its length. The middle portion of the column then turned into a “satellite” droplet (Figure 2, 104).

The secondary droplet landed on the surface but did not immediately coalesce (Figure 3, 200). Instead, the sequence described above in association with Figure 2 repeated itself. Cycles of residence and coalescence repeated several times, and after each coalescence event, a progressively smaller droplet was produced. Each such droplet jumped upward (360, 405). The smaller the droplet, the higher it jumped. The highest jumps were approximately 5 to 6 mm, close to the height from which the original droplet was released.

The sequence of coalescence steps is referred to as “coalescence cascade.” For clarity, we refer to the original droplet as the “primary”, whereas the daughter droplets are referred to as “secondary”, “tertiary”, and so on. In the majority of trials, six residence-coalescence cycles were observed.

The diameters of successive droplets in the stepwise cascade are presented in Figure 4. During each step, the diameter diminished to ~ 0.6 of the initial diameter. The exception was the first step, when the ratio was ~ 0.4 . The reason for this lower value may be that during the first step two daughter droplets were sometimes produced instead of one, as previously mentioned. The one that remained in place was regarded as the secondary; the other had a smaller diameter (0.3 to 0.5 mm) and frequently shot off to one side. The graph in Figure 4 shows up to fifth-order droplets, but sixth-order droplets were present as well, although they were too small to be accurately measured.

The time that a droplet resides on the bulk prior to coalescence is referred to as the “residence time.” Droplet-residence times are presented in Figure 5. Residence time diminished with the droplets’ size. Therefore, primary droplets were longest-lived, with residence time averaging 143 ± 9 ms ($n = 30$). Secondary droplets persisted for 78 ± 35 ms, and higher order droplets persisted for progressively shorter times. The residence time of each droplet was commonly 0.7 of that of the preceding droplet.

In the majority of trials, the pattern of primary droplet coalescence was not symmetrical; that is, secondary droplets typically jumped obliquely. Also, coalescence of primary droplets initiated waves on the bulk-water surface. Therefore, secondary droplets landed on a perturbed water surface rather than on a still surface and hence moved sideways. This affected both stability and residence time of secondary droplets, which is reflected by the high residence-time standard deviation (Figure 5, bar 2). Sideways displacement occurred for all droplets in the cascade; however, droplets of higher order were smaller, and thus their coalescence produced smaller distortions of the bulk surface.

3. Moving Droplets

Whereas sideways drift was commonly seen in secondary droplets, primary droplets occasionally drifted sideways as well. Among those that drifted noticeably, drift velocities typically ranged between 3 and 13 mm/sec. These drifting droplets had residence times of 608 ± 132 ms ($n = 50$). This should be compared with residence times of stationary primary droplets, whose mean value (above) was 143 ms, approximately four times longer than the persistence of stationary droplets.

Droplets with sideways drift could easily be produced by allowing water to flow freely down through the nozzle. This was achieved by disconnecting the Tygon tubing from the syringe so that a continuous water jet formed between the nozzle and the bulk surface. Occasionally, the jet broke into individual droplets, which often landed on the surface in

rapid succession without coalescing (Figure 6). The droplets appeared in a variety of sizes ranging between 1 and 3.5 mm, at a rate of 3–5 droplets per second. If a large droplet happened to be residing just beneath the nozzle, then successive droplets slid down the residing droplet's surface, landing on the bulk water without coalescence and continuing to move sideways. Smaller droplets generally moved faster than the larger ones. Therefore, 1 mm droplets moved at 209 ± 67 mm/s ($n = 10$), whereas 3 mm droplets moved at 46 ± 20 mm/s ($n = 12$).

Analysis of residence times versus translation speed of these droplets revealed no apparent correlation. As long as droplets moved, their residence times were enhanced relative to non-moving ones but in seemingly random fashion with regard to velocity. Size did play some role: larger droplets persisted longer than smaller ones (Figure 7). The graph shows a roughly linear correlation of residence time with diameter, and, with mean residence time of 518 ± 263 ms, compared with ~ 140 ms with nonmoving droplets, the result confirms again that on average moving droplets persisted longer than stationary ones.

4. Residence-Time Consistency

During the initial experimental runs measured, residence times were inconsistent. Not only were they inconsistent within a series (Figure 8, dark bars) but also different series produced different degrees of inconsistency. In some experimental series, all droplets coalesced immediately upon contact.

Reasons for inconsistencies were further explored by the addition of electrical and mechanical perturbations to the system. To test for mechanical disturbances, the entire setup was moved onto a vibration-isolation table, with no observable difference in results. To test for inconsistencies originating from minor variations in experimental procedure, the protocols prior to and during each experiment were strictly maintained; again, there was little observable change. In some experiments, the purified water was passed through a fine filter (Whatman Nylon $0.2 \mu\text{m}$) to eliminate any microscopic particles that might have been present, but this procedure also had no apparent effect on reproducibility.

We also considered residual electric charge. The impact of electrostatic charge was confirmed by bringing a charged glass rod near the nozzle. With the charged rod nearby, the primary droplet-residence time diminished sharply to ~ 50 ms, and secondary drops were not seen. With electrostatic fields implicated as potentially relevant, we found that the one procedure that did make a difference in terms of consistency was grounding both the nozzle tip and the bulk water. This was done by connecting both the water-supply tube and the base of the setup to a common building ground. This procedure resulted in consistency such as that shown in Figure 8 (light bars).

Another factor contributing to the inconsistency was found to be water-surface purity. When some residue (dust, grease) was purposely left on the glass substrate prior to the addition of water, floating droplets often did not form at all. Bubbles of air trapped in the nozzle or water-supply line also caused inconsistencies and diminished residence times. As the droplet grew at the tip of the nozzle, the water flow partially shifted the air bubble downward to outside the nozzle. When the droplet detached, the bubble then retracted back to the nozzle. When such bubbles were present, the residence times were less consistent.

In sum, realization of consistency depended on careful control of a number of factors. Once these factors were identified and controlled, experimental results could be obtained on a consistent basis. All experiments reported above and below were carried out with these factors under control.

5. Abrupt Residence-Time Change

In some trials, residence time suddenly switched from one stable value to another. An example is shown in Figure 9. Residence times of the initial group of droplets were ~50 ms. After the 15th droplet, residence time jumped to 160 ms and stayed at approximately that value for some time. Then, it jumped back to 50 ms, only to return to the higher value after the 26th droplet.

Such bimodal behavior was observed in ~10% of all recorded series. From the recorded videos, we could find no visual indications of any differences in the setup, the droplet size, or the way droplets formed during these abrupt residence-time shifts. In Figure 9, the two residence times were 53 ± 8 and 164 ± 14 ms; they were separated by eight SDs. Of the five such records examined, the average separation was 5.8 standard deviations.

6. Effect of Nozzle Height

Nozzle height was increased from 5 to 10 mm in 1 mm increments and then from 10 to 18 mm in 2 mm increments. At each height, 20 droplets per trial were observed in three separate trials. For droplets released from heights 5 to 10 mm, primary residence time did not vary appreciably from the ~140 ms reported above. At heights of 12–16 mm, most droplets coalesced shortly after impacting the bulk surface, with residence times between 0 and 30 ms. However, droplets that were able to survive the initial impact usually persisted on the surface for ~120 ms. At 18 mm and above, coalescence occurred instantly.

When a very thin (1 to 0.5 mm) layer of bulk water was used on the receiving surface instead of the standard-thickness layer, the behavior of droplets was different. The layer was created by first dispensing 10 mL of deionized water on the glass slide and then removing most of the water with a needle attached to the house vacuum. Only a thin wetting layer remained on the glass. Droplets were then released from a 10 mm height. After the impact, droplets flattened as though they were hitting a solid surface and then recoiled back up to a height ~4 mm above the surface (Figure 10). The droplets bounced two to three times, the height diminishing with each cycle. Sometimes, a water bridge was visible between the droplet and the bulk during the initial portion of the bounce (Figure 10, 60 ms inset), which disappeared within one or two frames (5–10 ms). Between the bounces, no reduction in droplet size was noticed. When the droplet came to rest, it coalesced after ~150 ms.

7. Effect of Reduced Air Pressure

To check the effect of air pressure on residence time, the pressure in the experimental chamber was reduced in 10 kPa increments from atmospheric pressure (~100 kPa) down to 10 kPa. Two sets of experiments were performed at each pressure. In one set, water was taken directly from the purification unit and used immediately in the experiment; in the other set, water was kept at the respective air pressure while being stirred for 1 h prior to use to produce “equilibrated” water. The need for this latter procedure arose particularly at relatively low air pressures when air bubbles began to appear in the water-supply line. With bubbles present, droplet production became sporadic and unpredictable. This problem could be averted through the use of the equilibrated water.

Residence time diminished linearly with diminishing air pressure (Figure 11). For the nonequilibrated water, 20 and 10 kPa data points are missing because bubbles upset the experiment. Residence times were slightly higher for equilibrated water than nonequilibrated water at all pressures, the difference being slightly more substantial at lower pressures.

The effect of pressure on the number of coalescence steps is shown in Figure 12. Median values are shown. The median remained constant at four in the higher-pressure range and

then diminished as pressure was reduced. At the lower pressures, secondary droplets were much smaller than those formed at atmospheric pressure and had residence times of 5–10 ms.

A noteworthy effect of the air-pressure change was that each time the pressure was reduced, the first few droplets coalesced instantly; then, longer residence times would gradually appear. Even when the pressure reduction was preceded by a pressure increase, the same effect appeared. Somehow, reducing chamber pressure temporarily upset the ability of water to form floating droplets.

Even at reduced air pressures, there were occasional droplets with surprisingly long residence times. On one occasion at 60 kPa, three consecutive droplets were observed with residence times of ~250 ms. Because there were only a small number of such droplets and their residence times were vastly different from the majority, they were considered to be exceptional and were not included into the mean residence time.

IV. Discussion

Under controlled conditions, purified water droplets falling onto a surface of similarly pure water do not coalesce instantly. Once the droplet hits the surface, it oscillates vertically several times before finally settling into apparent quiescence, extending from tens to hundreds of milliseconds. Then, coalescence begins abruptly. During the process, a liquid bridge forms, connecting the droplet proper with the water beneath. The droplet appears to expel water downward through this bridge. The lower neck of the bridge then pinches off, and a droplet smaller than the original one is left suspended above the surface.

Once this smaller droplet hits the surface, the pattern repeats, commonly up to five times. The number of steps needed for complete coalescence and the residence time both depended on such factors as droplet size, residual electrostatic charge, fall height, and air pressure. Interestingly, the residence times of successive droplets sometimes alternated between two relatively stable values under seemingly consistent conditions.

In addition to stationary droplets, side-moving droplets were observed under some circumstances. Such droplets translated along water's surface and required relatively longer times for coalescence, sometimes many hundreds of milliseconds. Some of these moving droplets coalesced in multiple steps, whereas others did so in one step.

1. Previous Work on Noncoalescence

Delayed droplet coalescence is not a new phenomenon, although, surprisingly, few scientists seem aware of it. The first published observations were made by Rayleigh,⁶ who observed that droplets of water often bounced off one another, whereas Reynolds^{1–7} subsequently observed droplets floating on flat liquid surfaces. A major contribution was made by Mahajan,⁸ who studied the noncoalescence phenomenon with various liquids under controlled conditions. Each liquid had so-called “critical height.” Droplets released from above that height always coalesced instantly, whereas those released from below that height showed noncoalescence. Also, the ability of liquids to form floating droplets depended on the liquid's viscosity and surface tension. In particular, with solution of phenyl in water and “Boys' soap” solution (2.5% sodium oleate and 25% glycerine in water), the critical height depended on the amount of solute in the water. Despite success with these solutions, pure water droplets falling onto water instantly coalesced.

Research into noncoalescence was taken a step further by another group⁴ who focused on situations when droplet and bulk liquids were different. When different liquids with long

polar molecules (molten fats, paraffin, drying oils) were used in droplets and in the bulk, floating droplets were readily produced. When the droplets contained smaller molecules, they coalesced instantly. Liquids with relatively similar molecules showed dramatically different abilities to form floating droplets depending on the arrangement: with a consistent pair of particular liquids, floating droplets could often form when one liquid was used in the drop and the other in the bulk, whereas reversing the liquids resulted in instant coalescence. Water was again reported as incapable of producing floating droplets. Indeed, water has been considered to be a “poor” candidate for producing noncoalescing droplets, and hence the number of studies dealing with droplets of pure, deionized water has been limited.

A number of studies have recently dealt with the mechanism underlying the stepwise nature of coalescence.^{9–11} One idea is that the bridge that connects the droplet with the bulk becomes unstable, thereby interrupting coalescence and requiring multiple steps for completion.¹² Another hypothesis comes from high frame-rate imaging of coalescence events, which revealed capillary waves traveling upward along the droplet’s surface in the first moments of coalescence.¹³ When these capillary waves meet atop the coalescing droplet, they merge, seemingly producing the secondary droplet. From this observation, the authors conclude that if a layer of surfactant was present on top of the liquid surface, then the capillary waves would dampen, thus inhibiting stepwise coalescence. Theoretical considerations based on the air-cushion hypothesis¹⁴ lead to the conclusion that a layer of surfactant should not inhibit noncoalescence but should in fact be a necessary condition for its existence. Overall, considerable debate still exists on the mechanism underlying the coalescence cascade.

Under certain conditions, noncoalescence can achieve semipermanence. When a significant temperature gradient is maintained between droplet and bulk, noncoalescence can be maintained indefinitely.¹⁵ Permanent noncoalescence can also be created by setting the bulk surface into a continuous motion through shaking¹⁶ or by stirring or blowing air over the surface.^{17,18}

An additional factor affecting droplet dynamics is charge, which has been long identified as a major inhibitor of noncoalescence.^{6,8,12} The effect of charge was first described by Rayleigh, who observed that colliding droplets tended to coalesce more readily when an electric field was present.⁶ In recent experimental work,¹⁹ a layer of oil was created on top of bulk water, and water droplets submerged in oil were allowed to sink down through the oil and pass onto the bulk-water. When a potential difference was applied vertically across the experimental chamber, the droplets did not coalesce, even when a clear liquid bridge formed, connecting droplet and bulk. Therefore, electric fields can either promote or extinguish noncoalescence.

Regarding the effect of air pressure, occasional observations made decades ago showed that the formation of floating water droplets could not be achieved at normal atmospheric pressure but was possible at higher altitudes where the pressure was lower.^{2,8} More recent studies with silicone-oil droplets confirmed the increase in residence time at low air pressures.^{3,18}

2. Air-Cushion Mechanism?

According to a recent review,²⁰ the currently favored hypothesis for explaining the absence of instant coalescence is that a layer of air is entrapped between the droplet and the bulk surface, preventing coalescence until the air has drained away. The most direct evidence of this hypothesis comes from interferometry data,²¹ which demonstrates the existence of a distinct layer between a heated silicone-oil droplet and a glass surface pressed against one another. This layer is presumed to be air. Additional supportive evidence comes from the

observed formation of Newton's rings beneath noncoalescent droplets.^{16,22} The rings are thought to originate from multiple reflections and interference of light between droplet and bulk surfaces, separated presumably by a layer of air.

The air-cushion hypothesis seems out of accord with several phenomena reported here and elsewhere. First, within a droplet-release series, we found that under seemingly identical conditions the behavior of droplets could change back and forth from noncoalescence to instant coalescence. Even when conditions were controlled to optimize repeatability, instant-coalescence events were still occasionally interspersed between delayed coalescence events. Why the air would get trapped beneath one droplet but not another is difficult to envision.

Second, although diminished air pressure diminished the residence time, the expectation of the air-cushion hypothesis¹⁸ is that at zero pressure residence time should converge to zero, but that was apparently not the case (Figure 11); residence time remained substantial. In fact, some long-lasting droplets were observed even at very low pressures. Diminished air pressure also impacted the number of steps required for full coalescence, another feature difficult to fit naturally within the framework of the air-cushion hypothesis.

Another issue is the phenomenon of abrupt residence-time change. Residence time could take on a consistent value for a succession of hits and then suddenly take on a new consistent value that was appreciably different, sometimes by a factor of 2 (Figure 9). Residence time could sometimes oscillate between the two values. If coalescence was delayed because an air cushion needed time to vanish, then it is not clear why residence time should vary between two seemingly discrete values.

Finally, the residence time of moving droplets was longer than that of nonmoving droplets. If an air cushion were trapped between droplet and surface, then as the droplet moved from its initial position, any air trapped between droplet and surface should quickly vanish. Yet, residence time did not diminish in the moving droplets but actually increased, sometimes substantially (Figure 7).

3. Toward an Alternative Mechanism

Previously unrecognized features of water revealed in recent reports may bear on the mechanism of noncoalescence. A recent X-ray spectroscopy study shows that bulk water consists of large clusters of structured water surrounded by less-organized bulk-water molecules.²³ Such clusters are implied by AFM studies also at the air–water interface,²⁴ where self-organization into more extensive and robust structures is possible. Therefore, the zone of water interfacing with air could differ substantially from the bulk.

This interfacial layer may be extensive. Recent results from this laboratory show an interfacial zone extending down from the surface sometimes by up to hundreds of micrometers or more, enhanced apparently by incident infrared radiation and also by oxygen.^{5,25} The presence of a substantial interfacial layer could work as an effective barrier that prevents instant coalescence.

A possible mechanism based on the presence of this interfacial layer is illustrated in Figure 13. Before droplet and bulk come into contact, both entities are presumed to have significant interfacial layers (1), which prevent immediate coalescence (2). Once they touch, the interfacial layers begin to dissipate (3). When the layers have dissipated sufficiently, coalescence begins, and water from the droplet begins to flow downward (4). As the water evacuates, the droplet diminishes in volume, creating a narrower entity between the droplet and the bulk (5). The pinch-off creates the daughter droplet (6). The process then repeats, perpetuating the cascade.

Within this mechanism, a number of experimental observations seem to be explainable. First are the observations of Newton's rings and interferometric data, both of which imply separation. Here the separation arises not from entrapped air but from the interfacial layers, whose optical properties presumably differ somewhat from those of bulk water.

The second is that coalescence occurs in stepwise fashion (Figure 3). That is, the merger of droplet and bulk is repeatedly interrupted. During coalescence, the interfacial layers beneath the droplet are presumably depleted for the water to flow from droplet to bulk, but they must rebuild if the sequence is to recur, and this process may take time. Repeated breakdown and rebuilding would then explain the stepwise nature of coalescence.

The third observation is that sliding droplets had longer residence times than those that were stationary (Figure 7). For similarly sized droplets, the difference could extend up to six times. This difference could follow from the need for interfacial layers to fuse: whatever coalescence-promoting reaction takes place between droplet and bulk might proceed readily if the droplet were stationary, but with movement, the respective surfaces would no longer be in juxtaposition and the reaction could easily take much longer.

A fourth point is that residence time diminished with diminishing air pressure (Figure 11). If the amount of available oxygen determines the thickness of the interfacial layer (Marshall et al., in preparation), then the reduced oxygen present at lower pressures would result in thinner interfacial zones and hence shorter residence times and fewer steps in coalescence cascade.

Whereas the hypothesis accounts for the main observations, a number of other observations remain to be explained. For example, the explanation for abrupt residence-time change is yet unclear. A possibility is that the interfacial layer is a patchy mosaic, as implied from infrared imaging of the bulk surface.²⁶ Hence, a droplet might persist when falling on one phase of the surface but might not persist as long when falling on the other. This might also explain why some droplets coalesced instantly whereas others did not (Figure 8).

Another observation not yet explained is why the water inside the droplet moves rapidly downward into the bulk during coalescence. Whereas this movement might occur passively by gravitation, the rapidity hints that some kind of pressure may build within the droplet, propelling the liquid into the bulk. The mechanism underlying any such movement is unclear.

Finally, it is unclear why following abrupt pressure reduction, the first few droplets in a series coalesced instantly, whereas subsequent ones showed coalescence delay. A possibility is that the sudden pressure reduction creates microbubbles beneath the bulk-water interface, which remain to disrupt the interfacial layer for some time. However, this is merely a speculation, which remains to be tested.

Overall, the phenomenon of stepwise coalescence evidently requires additional study. Even if the hypothesis outlined above proves to be adequate, it is evidently incomplete and requires further development. Many natural and technological processes involve droplets of liquid colliding with liquid surfaces, including rainfall, spray systems, cooling systems, combustion engines, microfluidics, and inkjet printing, processes that could benefit from a deeper understanding of droplet coalescence. Such studies could also provide a vehicle for gaining understanding of the characteristic properties of the liquids themselves. That includes water, whose properties are still surprisingly enigmatic.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Schematic representation of experimental setup.

Figure 2.

Dynamics of water droplet falling onto water surface. Numbers indicate time count in milliseconds. White spots on the droplet are reflections of the illuminating light and should be ignored. Reflections of droplet on water surface and on microscope slide underneath are also visible. For optimizing presentation, the frame rate here was increased to 250 frames per second.

Figure 3. Coalescence cascade. For reference, the primary droplet is shown in the top left corner. The numbers indicate time in milliseconds after the primary droplet detached from the nozzle. For easy visualization, the trial displayed is one in which sideways motion of droplet was relatively small. A movie demonstrating coalescence process is available in the Supporting Information.

Figure 4. Average droplet diameter in coalescence cascade. Droplet order refers to primary droplet, secondary droplet, and so on. ($n = 30$ coalescence cascades).

Figure 5.
Residence times of droplets in cascade.

Figure 6. Floating droplets formed as the jet of water from the nozzle broke into individual droplets. Floating droplets quickly translated away from the region immediately beneath the tip.

Figure 7.

Residence times of randomly chosen moving droplets with different diameters ($n = 55$, from four experimental trials). Residence times were measured from the moment of droplet formation in the vicinity of the nozzle until the first coalescence step.

Figure 8. Comparison of trials with inconsistent (darker) and consistent (lighter) primary residence times. Where no bar is present, coalescence was instantaneous upon contact.

Figure 9. Residence time versus droplet number, with examples of abrupt residence-time changes.

Figure 10.

Water droplet bouncing on a thin layer of water. Inset shows apparent water bridge between droplet and surface. The impact flattened the droplet and produced surface waves visible on the 50 ms panel.

Figure 11.
Influence of air pressure on residence time.

Figure 12. Effect of air pressure on the number of steps in coalescence cascade. Median values are shown at each pressure.

Figure 13.
Possible mechanism of delayed coalescence.