



Whiskey webs: Fingerprints of evaporated bourbon

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When a water-diluted droplet of American whiskey evaporates, it can leave behind a self-assembled web pattern not found in Scotch or brandy.

Did you know that there are colloids in bourbon? That question came from a research engineer at Brown-Forman Corporation in Louisville, Kentucky—a state with nearly twice as many aging barrels of bourbon as people—when I was touring the corporation’s research facilities a few years ago. Most consumers expect a clear, rich amber color in their bourbon. And to ensure that quality, manufacturers usually monitor their whiskey’s turbidity, or cloudiness. Colloids often form when whiskey is diluted with water, though the contents usually remain soluble if the mixture exceeds 46% alcohol by volume (ABV).

Lower dilutions are filtered using charcoal or by what’s known as chill filtration. But the process is largely an art, considered part of the whiskey’s recipe, and may affect its final color and flavor profile. Interested in learning more, I acquired a variety of aged whiskeys from Brown-Forman to investigate the fundamentals of whiskey colloids. At the time, I was preparing for a sabbatical at North Carolina State University to study with colloid scientist Orlin Velev, and I reasoned that arriving at his lab with a case of whiskey in hand would make a good first impression.

Evaporation dynamics

During our investigations, Velev and I became interested in the behavior of evaporating droplets of whiskey. Howard Stone’s group at Princeton University had studied the issue using evaporated Scotch whisky in 2016 and noticed that the evaporated droplets produced uniform films whose formation fundamentally differs from that of coffee-stain rings. The characteristic ring forms because the evaporation of a droplet is faster at its edges. Whereas the dark edges of the ring form as coffee grains drift outward and accumulate at the droplet’s pinned meniscus, Stone and his colleagues found that the fluid motion in a Scotch droplet actually counters that outward drift from differential evaporation. The presence of surfactants lowers the whiskey’s surface tension, and as the liquid evaporates, the surfactants collect on the droplet perimeter and pull the liquid inward—the so-called Marangoni effect.

We were curious if bourbon evaporation was comparable, as the two liquids are prepared differently. Whereas Scotch is stored in reused wooden barrels, bourbon is a type of American whiskey stored in new, freshly charred oak barrels and has a grain composition, or “mash bill,” of more than 50% corn. Furthermore, we had samples of different ages and wanted to see if we could distinguish them by their films.

We evaporated microliter droplets at 45% ABV, and they formed uniform films, just as in the Scotch study. Next, we

evaporated droplets of various dilutions. Some whiskey enthusiasts believe that adding water enhances whiskey’s aroma and taste, but it’s more universally known to hasten the transport of congeners—aldehydes, esters, phenols, and other fermentation products—to the surface and modify the whiskey’s interfacial properties. We prepared a collage of evaporated-droplet images at different proofs, shown in figure 1. At alcohol concentrations of 20–25%, strange patterns emerged; none had appeared in the Scotch study. Ever since, we have dubbed those evaporation patterns whiskey webs.

We spent the following months exploring the fundamental physics behind whiskey webs. First, we wanted to know when those structures formed. A 1 μ l droplet of diluted whiskey takes approximately 10 minutes to evaporate, during which several fluid-dynamic mechanisms occur, as illustrated in figure 2. In the first minute or so, Marangoni flows produced by the differential evaporation of ethanol in the droplet drive colloidal clusters—aggregates of insoluble congeners—to the liquid–air interface. There, the clusters break open into distinct chains that start forming a self-assembled monolayer.

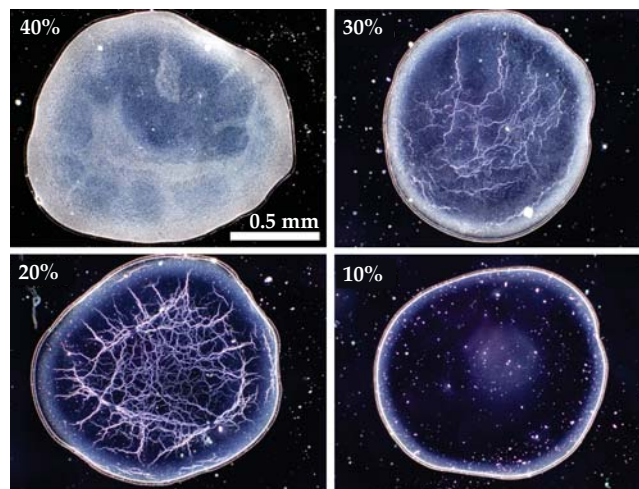


FIGURE 1. WHISKEY WEBS. Some of our first images, created from the evaporation of 1 μ l of diluted Jack Daniel’s bourbon on a clean glass coverslip. At high proofs—that is, high alcohol by volume—the evaporated drop forms a uniform film; at intermediate proofs of 20–25%, the intricate folds of a whiskey web forms; and at low proofs, coffee-ring patterns form. Brightly lit lines indicate the collapsed folds in a self-assembled monolayer of water-insoluble chemicals in the bourbon. (Images from Stuart Williams.)

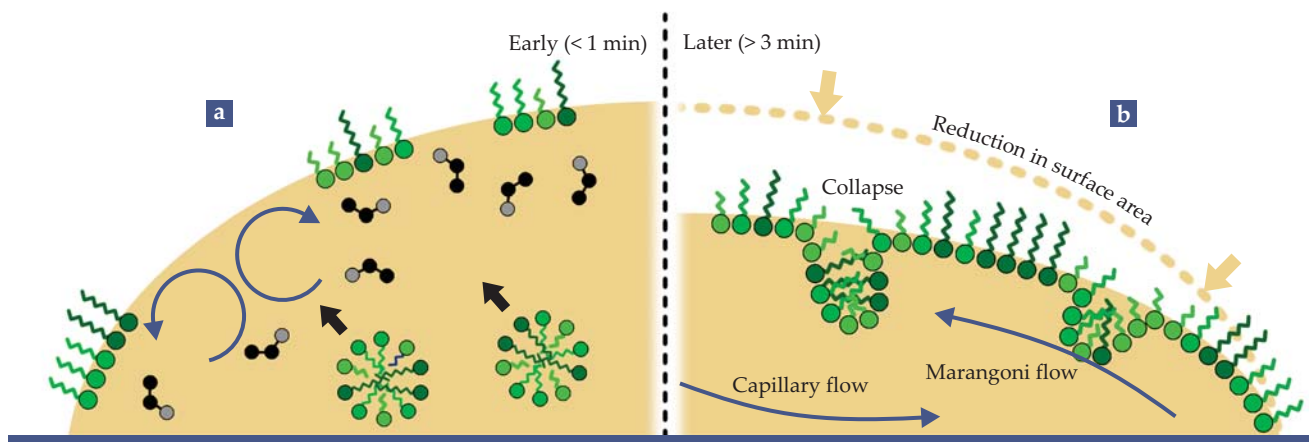


FIGURE 2. FLOW, SELF-ASSEMBLY, AND COLLAPSE. As whiskey is diluted in water and deposited on a glass coverslip, it starts evaporating. **(a)** Marangoni flow initially dominates, driven by the differential evaporation of ethanol (black). The flow and concomitant erratic vortices (blue) carry colloidal clusters to the surface–air interface, where they open into chains of fatty acids (green) that start assembling into a monolayer. **(b)** As evaporation continues, the droplet’s surface area decreases by 30% or so and stress on the monolayer causes parts of it to fold and eventually collapse. (Adapted from A. D. Carrithers et al., *ACS Nano* **14**, 5417, 2020).

To visualize the bulk fluid motion, we added fluorescent microparticles to the sample and monitored them during evaporation. Erratic vortices typical of ethanol–water mixtures also emerged during that first minute or so. In the second phase of evaporation, surface-tension-driven Marangoni flow is still at work, along with capillary flow toward the droplet’s edge. Liquid evaporates more quickly there, and capillary flow compensates by driving fluid from the bulk to the perimeter. (See the article by Roberto Zenit and Javier Rodríguez-Rodríguez, *PHYSICS TODAY*, November 2018, page 44.)

Visualization, tests, and reproducibility

The web structures began to form at the droplet’s liquid–air interface about halfway through evaporation. Seeing the patterns was easiest with scattered light, and we were able to monitor their formation using phase-contrast microscopy. The webs did not translate or rotate; the rigid structures remained on the surface during evaporation. Web density also increased as the surface area dropped. We hypothesize that a chemical monolayer forms at the liquid–air interface and subsequently folds and collapses from stresses imposed by the reduced surface area.

We tested 66 off-the-shelf American whiskeys, 56 of which were bourbon whiskeys. All but a 42-year-old sample formed webs at 25% ABV. The exception likely had elevated levels of surfactants, which are known to reduce the rigidity of monolayers. Indeed, no whiskey webs formed when we added a common surfactant (sodium dodecyl sulfate) to our bourbon. And some of our older whiskeys had fewer collapsed structures near the perimeter, behavior we believe is caused by a local elevated concentration of surfactants. Such surfactant gradients are known to drive Marangoni flow.

Unaged whiskey did not form webs in our experiments, nor did other non-American whiskeys. Because they are aged in charred oak barrels, American whiskeys typically have about twice the mass of suspended solids as other whiskeys. That aspect of production is likely key to understanding the uniqueness of American whiskeys in forming web patterns. Nonetheless, preliminary results suggest that other whiskeys *can* form webs, albeit under different conditions: A Canadian whiskey and an Irish one, for instance, formed structures in a 2 μ l droplet at 40% ABV. Using a lower dilution with a hydrophobic surface

increases the concentration of water-insoluble interfacial species and thus the likelihood of monolayer formation and subsequent collapse.

The complex flavor profile of whiskey is the result of its intricate composition of chemicals and congeners. That heterogeneity is also responsible for distinctive web patterns. For example, more lines form when a whiskey is spiked with lignin—a chemical associated with maturation in oak barrels. Other distinct modifications in the pattern emerged with the addition of other chemicals associated with flavor and maturation.

Those distinct patterns can be used to identify samples and counterfeits. As a demonstration, my group created 10 whiskey-web patterns from the same batch of whiskey and used digital image processing to map web density as a function of radial location in the droplet. We then repeated that process for two other whiskeys to generate a digital library. To test how well a pattern matched the whiskey used to create it, 15 droplets of each whiskey were evaporated, photographed, and compared to the library. Remarkably, a successful match was made 90% of the time. We believe that more robust digital-image algorithms—perhaps incorporating machine learning—may improve the technique.

What’s more, those whiskey-web images can be acquired using a smartphone camera. They might even provide distillers with an inexpensive means to conduct quality control.

To learn more and for advice on reproducing our results, see whiskeywebs.org.

Additional resources

- H. Kim et al., “Controlled uniform coating from the interplay of Marangoni flows and surface-adsorbed macromolecules,” *Phys. Rev. Lett.* **116**, 124501 (2016).
- B. C. G. Karlsson, R. Friedman, “Dilution of whisky—the molecular perspective,” *Sci. Reports* **7**, 6489 (2017).
- S. J. Williams, M. J. Brown VI, A. D. Carrithers, “Whiskey webs: Microscale ‘fingerprints’ of bourbon whiskey,” *Phys. Rev. Fluids* **4**, 100511 (2019).
- A. D. Carrithers et al., “Multiscale self-assembly of distinctive weblike structures from evaporated drops of dilute American whiskeys,” *ACS Nano* **14**, 5417 (2020).

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