Gallery of Fluid Motion

Yarning droplets: Marangoni bursting with a partially soluble component

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(Received 16 June 2022; published 7 November 2022)

This paper is associated with a video winner of a 2021 American Physical Society's Division of Fluid Dynamics (DFD) Gallery of Fluid Motion Award for work presented at the DFD Gallery of Fluid Motion. The original video is available online at the Gallery of Fluid Motion, https://doi.org/10.1103/APS.DFD.2021.GFM.V0073.

DOI: 10.1103/PhysRevFluids.7.110509

Depositing multicomponent droplets on a substrate can occasionally lead to intriguing and altogether unexpected phenomena. Salty colloidal water droplets on a flat surface exhibit intricate patterns of salt crystallization, as well as monolayer formation of colloidal particles, as the evaporation advances [1–3]. Colloidal droplets, deposited on a layer of saline water, form a corrugated ring-shaped deposit, which resembles a flower [4]. Similar flowerlike patterns were found to be Marangoni stress driven [5] in a droplet containing a surfactant, deposited on a liquid layer, and ultimately a binary water-alcohol droplet on top of an oil layer burst into a plethora of tiny droplets, i.e., Marangoni bursting. This recently found phenomenon [6,7] is as mesmerizing after 1000 times as it was the first time we saw it. The binary droplet will spread out into a thin droplet when it comes in contact with the oil-air interface. In such a shallow droplet, the evaporation rate will be highest at the outer rim [8,9], and as alcohol evaporates faster than water, a radial concentration gradient develops, with a higher water concentration at the edge of the droplet compared to the center. Since water has a higher surface tension than alcohol, a radial surface tension gradient emerges, driving an outward Marangoni flow. Liquid accumulates at the retracting droplet's rim, which becomes unstable and starts to shed small so-called daughter droplets.

The three components of the Marangoni bursting effect (water, alcohol, and vegetable oil) have similar refractive indices and the length scales of the phenomenon are very small (submicrometric at times). Therefore, imaging the phenomenon with sufficient contrast for visualization can be very challenging. One solution is to add dye to the binary droplet, as has been done in several previous works [6,7,10]. While highly effective in improving the imaging contrast, the dye can have non-negligible effects on the balance of interfacial tensions in the system [11]. Instead of dye, tracer particles at a sufficiently high concentration can also offer an improvement of imaging contrast. Depending on their material, some polymer tracer particles are stable in a binary water-alcohol solution and have seemingly no effects on the Marangoni bursting phenomenon. Other polymer particles, however, cannot withstand alcohol, for example, colloidal particles made of polymethyl methacrylate (PMMA), a rigid plastic which dissolves in isopropyl alcohol (IPA). The particles' dissolution leads to an entirely different effect than the previously described Marangoni bursting.

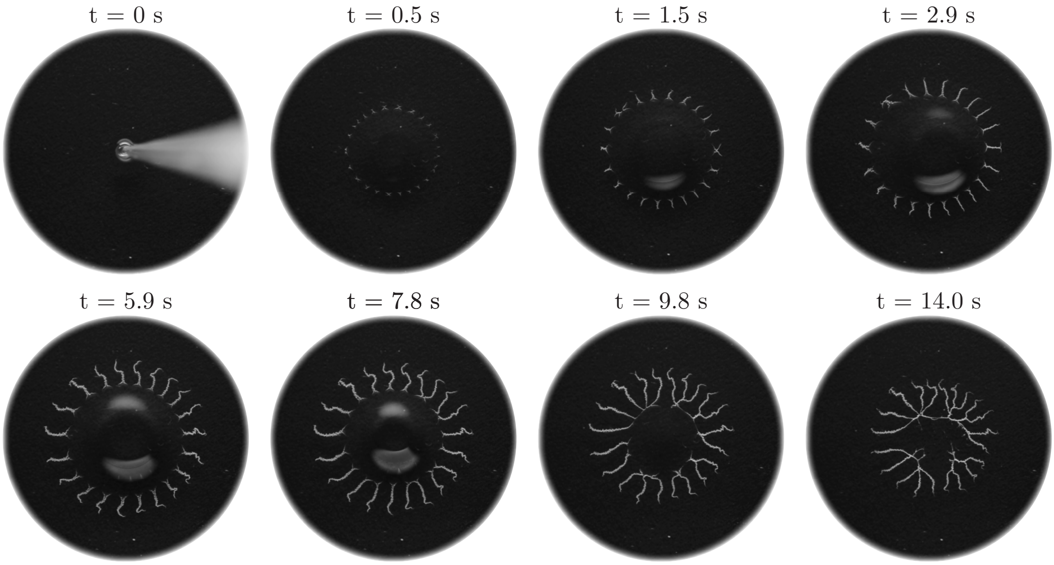

FIG. 1. Snapshots during the deposition, and subsequent spreading and evaporation, of a water-alcohol droplet (20% water, 80% IPA), laced with PMMA particles at a volume concentration of 0.1% in the original binary solution. The PMMA particles dissolve in the binary solution due to the high IPA concentration. In the mother droplet, the dissolved PMMA is transported by the outward Marangoni flow to the droplet rim. The IPA concentration at the rim is low enough for the PMMA to precipitate. In the first image for t = 0 s, the pipette tip to deposit the droplet is visible. We place the droplet on top of a roughly 3-mm-thick sunflower oil bath in a Petri dish, which is placed on top of a black, nonreflective hard plastic. We illuminate the experiment with an LED light source from the side and take images from above with a standard DSLR camera and a 100-mm macrolens.

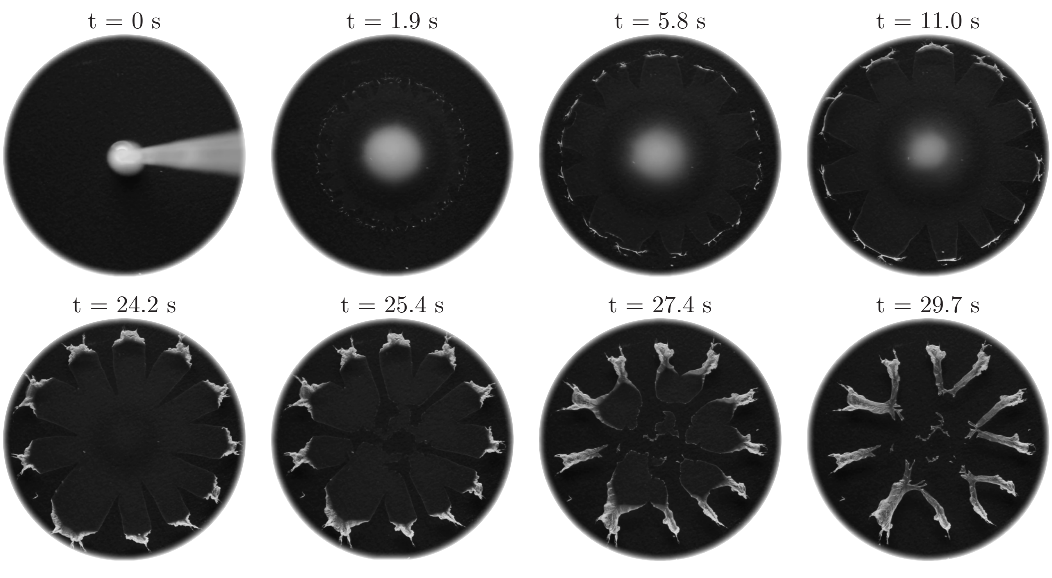

FIG. 2. Snapshots for a water-alcohol droplet (40% water, 60% IPA), laced with PMMA particles at a volume concentration of 0.1% in the original binary solution. The dissolved PMMA is transported towards the rim of the mother droplet, where the IPA concentration is low enough for the polymer to precipitate. The precipitation prevents any droplet shedding from the rim and instead creates a sheet, which cracks and finally splits up. In the first image for t = 0 s, the pipette tip to deposit the droplet is visible.

Instead of disintegrating into myriads of smaller droplets, the mother droplet starts to develop thin, almost tentaclelike threads at the edge (see Fig. 1), if the initial IPA concentration is high enough.

The PMMA particles dissolve in the binary solution, and when the mother droplet is deposited on the oil and spreads out, the dissolved polymer is transported towards the droplet's rim by an outward Marangoni flow [6]. At the rim, the alcohol concentration is low enough for the polymer to precipitate again. Instead of daughter droplets pinching off of the rim, fine threads of folded, precipitated PMMA are extending radially outward, like yarns of wool being spun from a distaff.

For a lower initial IPA concentration, we observe a slightly different mechanism (Fig. 2), in which the precipitated PMMA forms a sheet in the outer region of the droplet, which then cracks from the rim radially inward. Towards the end of the droplet's lifetime, when the IPA presumably is all but gone, the center of the droplet sheet also ruptures and the precipitated polymer sheet crumbles and folds in on itself.

There are still many open questions about this phenomenon of the *yarning droplet*: What is the exact mechanism for the polymer sheet formation? How does it rupture and what determines the rupture locations? Which parameters govern the folding site wavelength of polymer threads along the perimeter of the droplet? How does the precipitation prevent the shedding of daughter droplets completely? There are many details about this system still unknown, but it offers new fascinating prospects to chase after, perhaps leading to methods to investigate solutal concentrations [12]. In any case, the beauty and apparent simplicity of the phenomenon shown here will surely motivate a more in-depth investigation in the future.

The authors acknowledge financial support from the European Research Council, Starting Grant No. 678573 NanoPacks.

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