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Coffee Rings and Coffee Disks: Physics on the Edge

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Abstract

As many a coffee drinker knows, a drying drop of coffee typically leaves behind a ring-shaped stain of small grounds. Though the phenomenon is common, the mechanisms that drive it are rich with physics. As first elucidated by Robert Deegan and colleagues in 1997, the coffee ring results from radially outward fluid flows induced by so-called contact line pinning: The outer edge of a spilled coffee droplet grabs onto rough spots on the solid surface and becomes pinned in place. The evaporating drop thus retains its pinned diameter and flattens while it dries. That flattening, in turn, is accompanied by fluid flowing from the middle of the drop toward its edge to replenish evaporating water. Suspended particles—the coffee grounds—are carried to the edge of the drop by that flow. Once there, they pile up, one at a time, into a tightly jammed packing and produce the coffee ring. Deegan and company studied the ring growth empirically by following the individual frames in a video of plastic colloidal spheres suspended in an evaporating droplet.

Disciplines

Physical Sciences and Mathematics | Physics

Coffee rings and coffee disks: Physics on the edge

Peter J. Yunker, Douglas J. Durian, and Arjun G. Yodh

The stains left by drying coffee would look quite different—both microscopically and macroscopically—if the suspended grounds weren't roughly spherical.

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Dried drops of ellipsoids

What happens when the shape of the suspended particles is altered? At first glance, it may appear that nothing should change. Ellipsoids, like spheres, will get caught up in radially outward flows and pushed to the pinned edge of the drop. However, when ellipsoids reach the edge, they do not pack densely. Instead, they form a loosely packed network layer on the drop surface. That network grows in a fairly disordered way toward the drop center as more ellipsoids are pushed to the edge; with time, the network becomes ever more rigid and resistant to the outward directed, flow-induced forces. Thus, when evaporation finishes, ellipsoids can coat the entire area under the drop.

Fundamentally, the stains left behind by drying suspensions depend on how the suspended particles deform the wedge-shaped air–water surface near the drop edge. Spheres sit at the drop surface without disturbing it. Aspherical ellipsoids, however, deform the interface. Their elongated shape, in conjunction with surface-tension forces, causes the air–water interface to bend, as shown in figure 1.

That deformation increases the drop surface area and costs energy. Thus, when two ellipsoidal particles approach one another, the minimum-energy configuration is one for which the deformed regions associated with each particle overlap to reduce the total surface area. Effectively, the ellipsoids feel an attractive interaction, which is typically strongest at their tips. As a result of those well-known interfacial forces, called capillary interactions, the ellipsoids at the drop edge behave like sticky particles. (Spheres, by contrast, behave like billiard balls.) Further, more elongated particles induce larger deformations of the air–water interface and feel stronger attractions.

Shape-dependent growth processes

Particle stickiness profoundly affects the roughness of growth depositions near the drop edge. To appreciate how small changes in the attraction between particles can modify growth, consider a simple model based on the popular video game Tetris. In the game, various shapes fall from the sky to the ground, but the Tetris-inspired model considers only square blocks that flow radially to the pinned drop edge, where they grow a film deposit. If the blocks flow without spatial correlations, then each column grows independently. As a consequence, tall columns can be neighbors with short columns, and the top of the deposit is rough, as shown in figure 2a.

Billiard-ball-like spheres on the surface of a drying drop have weak lateral correlations. As a result, the roughness of

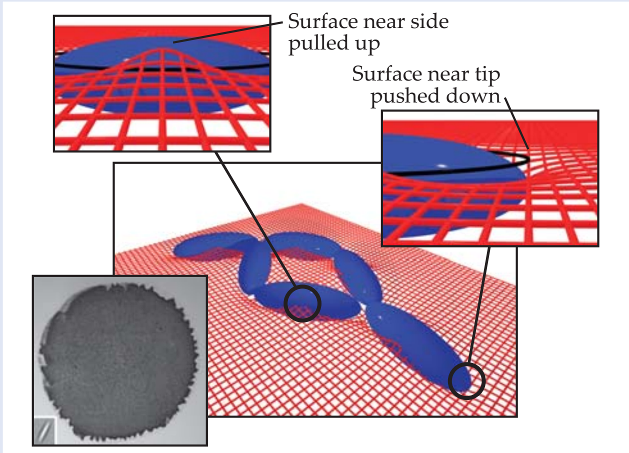

Figure 1. Ellipsoids deform an air–water interface by pulling the liquid surface up along their sides and pushing it down along their tips. Such surface bending effectively induces attractive interactions between ellipsoids and causes the particles on the air–water surface to form clumps. As a result, a drying drop containing a suspension of highly stretched ellipsoids leaves a disk-shaped residue, as shown in the photograph. The black rings around the two ellipsoids in the magnifications show where a flat, undeformed interface would meet the particles.

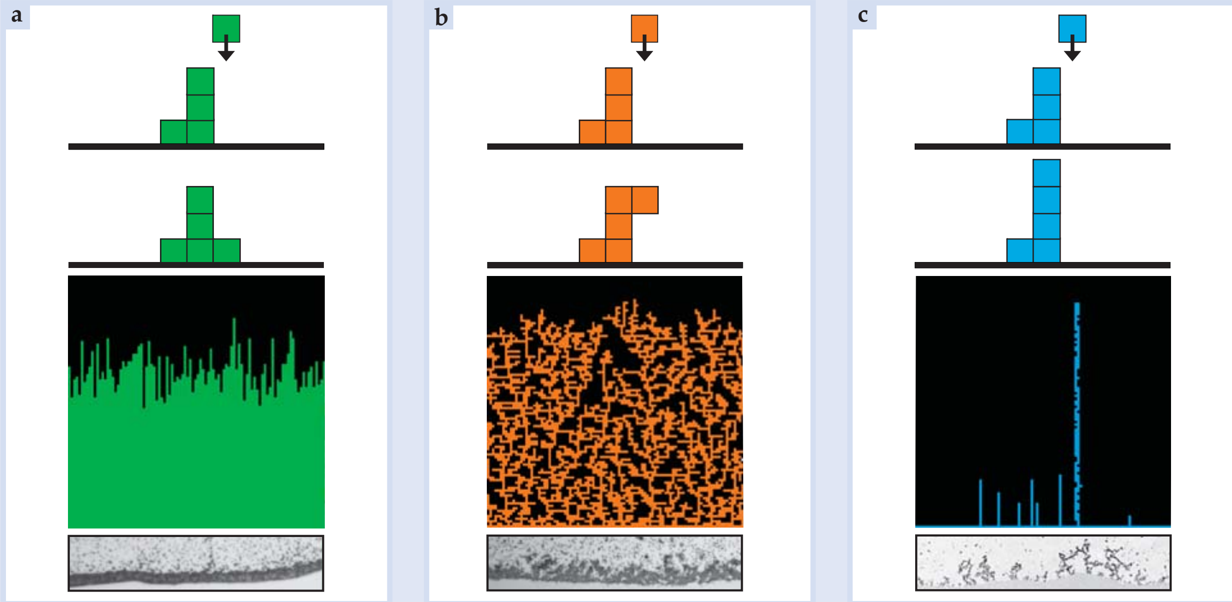

Figure 2. Growth processes for three different particle types may be modeled by a simple variation of the video game Tetris. The top colored figures in each panel schematically show the rules, described in the text, governing the growth of particles at the drop edge represented by the horizontal black lines. Below those images are simulated interfaces generated by the growth rules; the bottom of the simulation image represents the drop edge. The black and white photographs show the deposition of micrometer-sized polystyrene particles near the edge of a water drop as the drop begins to dry. **(a)** For spheres, each column grows independently, which causes the growth line defined by the tops of the columns to become rough—a tall column can be the neighbor of a short one. **(b)** Ellipsoids are sticky. If a not-too-elongated ellipsoid touches a tall neighboring column, it stops moving. As is evident in the photo, that effect causes the ellipsoids to clump. The resulting growth line along the column tops is relatively smooth. **(c)** Highly elongated ellipsoids are strongly attracted to other such particles on the air–water surface. Particles heading toward sparsely populated regions change directions and join large clumps of ellipsoids. Effectively, the growth rate increases in highly populated regions. The photograph shows the resulting very rough deposit, in which tall growth columns adjoin regions of zero growth.

the top of their growth deposit is substantial and increases as the film grows.

Films of ellipsoidal particles grow differently. The capillary interactions introduce a simple mechanism for lateral correlations. In the Tetris model, the now-sticky blocks still flow randomly to the drop edge, but when a particle touches a neighboring column, it sticks and stops moving; see figure 2b. The sticking enables short columns to quickly catch up in height with tall columns and smoothes the top of the deposit so that roughness increases more slowly than for spheres. The resultant growth, an example of a so-called Kardar-Parisi-Zhang (KPZ) process, was first introduced in a landmark paper as a solution to a simple growth model that includes nonlinear lateral correlations. KPZ processes occur when lateral interactions exist but are short range. In experiments with drying drops conducted earlier this year, we and other colleagues demonstrated that particles with a major- to minor-axis length ratio of about 1.2 grow deposits at the drop edge via the KPZ process.

If particles are strongly attracting, as is the case for highly stretched ellipsoids, then they will leave sparsely populated regions to join clumps of ellipsoids in highly populated regions; figure 2c shows the process as realized in the Tetris model. The phenomenon depicted there is a colloidal version of the Matthew effect: Particle-rich regions get richer, while particle-poor regions stay poor. The deposit is very rough, since tall regions can neighbor regions with no particles at all.

Growth lessons

The experiments and models discussed above have contributed to a new understanding of the complex nonequilibrium physics that affects particle deposition and growth. What can be done with the knowledge gained? The need for high-quality coatings furnishes one example. In applications such as painting a wall, printing a poster, or treating a pane of glass, uniformity is often of paramount importance. Experiments with suspensions of different particles show that thin, uniform coatings can be produced simply by choosing the right particle shape—ellipsoids. Perhaps more significantly, the growth processes exhibited by spheres and slightly stretched ellipsoids appear to belong to different universality classes. That's just a fancy way of saying that any system with the same deposition rules will grow in the same way, regardless of the microscopic details.

Furthermore, a wide array of different systems are members of the KPZ universality class. The advance of the combustion front on burning paper, the growth of certain bacterial colonies, and the development of the border between the ordered and disordered region of liquid crystals are examples of KPZ processes. Thus lessons learned from studying drying drops of nonspherical particles are relevant for other systems that, superficially, appear very different.

Additional resources

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