Say goodbye to coffee stains

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2012 Phys. World 25 (04) 33

(http://iopscience.iop.org/2058-7058/25/04/34)

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Discussing ideas over a mug of coffee or tea is the lifeblood of science, but have you ever thought about the stains that can be inadvertently left behind? H Burak Eral, Dirk van den Ende and Frieder Mugele explain how these stains, which can be a major annoyance in some biology techniques, can be altered for the better using a technique called electrowetting.

The headline of this article might look like a slogan for a cleaning product. You will be pleased to know that we are not trying to sell you anything, but the title does have a point: through our scientific interest in understanding coffee stains we have found a way to stop them forming in the first place. We are not talking here about the ring-like shape left behind by the bottom of a mug, but the smaller rings formed when individual puddles or droplets dry.

At first glance, stopping coffee stains from forming may seem unimportant – after all, they can be easily wiped up with a cloth. But the pattern they form when they dry is shared by other liquids, which get used in applications where the shape of the residue does matter.

Given the random nature of coffee-stain formation, residues form in different positions and with different shapes every time. For biologists and chemists who want to concentrate precious samples by evaporating droplets on a solid surface, crusty coffee-ring-like patterns ruin the efficiency and speed of their analyses. Often for these researchers, finding a bit of their sample that has a high signal-to-noise ratio is like searching for a needle in a haystack – they might use, for example, a laser with a tiny diameter to search a large area to find the most concentrated parts of the residue. Life would be easier for them if the sample dried as a small concentrated spot in one particular pre-assigned place: the researchers would then know exactly where to look and, moreover, would see a high signal for whatever parameter they are testing.

In striving to understand the underlying principles of coffee-stain formation, we have developed a way to counter the two key physical processes that cause the ring shape and can make droplets that instead leave behind a small, homogeneous dot. Moreover, our technique works not just for coffee but for any liquid with volatile and non-volatile components.

Non-volatile components studied using drying droplets are typically fragile molecules with a high molecular weight, which need to be treated gently to
Coffee-stain formation

Coffee spills during evaporation (left) and the characteristic stains they leave behind (right). A spilt droplet of a liquid with volatile (blue) and non-volatile (black) components, such as coffee, initially has a homogeneous distribution of non-volatile species. The edge of the droplet remains at a fixed position on the surface in what is known as contact-line pinning. At the edge of the droplet more of the volatile liquid can evaporate than at the centre, as there is more space for the volatile molecules to move into. This divergent evaporative flux causes a net flow of solvent (red) that transports non-volatile particles to the edge of the drop via viscous forces. As a result, the majority of the non-volatile species accumulate around the droplet edge, where they remain once all the liquid has evaporated (right). The black-and-white images show experiments by the authors that used 5µm-diameter fluorescently labelled polystyrene particles suspended in water, where the droplets dried on glass slides. The left-hand version is a time-averaged image where trails show the particle movement towards the droplet edge.

The coffee-stain phenomenon is more than just a nuisance – it is also a physical bottleneck for various industrial processes.
however, even the smoothest surfaces are rough on a very small scale. It is on these little cracks and dents that the edges of raindrops get stuck, i.e. where their contact lines get pinned.

When the contact line of an evaporating drop gets pinned, the edge of the drop assumes a wedge-like shape. Liquid molecules close to the tip of the wedge can evaporate more easily than those in the middle of the drop because they have more space available to move into. In other words, a liquid molecule at the tip of the wedge sees fewer neighbouring liquid molecules compared with a molecule in the centre of the drop. This leads to the diverging evaporation rate mentioned above. The large amount of evaporating liquid at the edge of the drop gets replaced by liquid from the middle of the drop. It is this net flow of liquid that transports suspended particles towards the contact line via viscous forces, where they remain to form ring-like shapes once all the solvent has vanished.

Despite the fact that the Deegan scenario ignores many details, it describes the essential physics of the phenomenon. But almost 15 years after this pioneering work, some aspects of the process still remain unclear, such as the influence of interactions between the solid, the droplet surface and the particles, as well as interactions among the particles themselves. Many scientists are trying to unravel the remaining mysteries and to find ways to prevent the formation of ring-like coffee stains.

When stains are a pain
The coffee-stain phenomenon is more than just a nuisance. It is also a physical bottleneck for various industrial processes that involve non-volatile components dispersed in evaporating solvents. One example is inkjet printing, which nowadays uses highly complex inks and is used in ways that go far beyond conventional printing. For instance, electronic circuits as well as organic light-emitting diodes (OLEDs) can be produced at low cost by depositing solutions of conductive and light-emitting polymers, respectively. In such applications, a homogeneous distribution of the non-volatile component is essential for the resulting devices to achieve high performances. Heterogeneous patterns such as rings are highly undesirable in these cases.

Another application where coffee stains make the lives of our fellow scientists miserable is a widely used analytical technique called matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS). This technique has a preparation stage (MALDI) and a detection stage (TOF-MS). In the MALDI stage the molecules to be detected, known as the analyte, need to be ionized. But since the molecules themselves are fragile and prone to damage, they must be treated gently. They are therefore first mixed with a salt solution, known as the “matrix”, and left to dry out. As it does so, the salt crystallizes, with the analyte located in and around the salt crystals. This crystallized residue is then subjected to a pulsed ultraviolet laser, energy which is absorbed by the matrix, with just enough energy then transferred from the matrix to the molecules to ionize but not fracture them. This “soft ionization” technique is particularly suited to biomolecules such as DNA, proteins, peptides, sugars and large organic molecules such as polymers and other macromolecules.

The detection stage of this workhorse technique involves pinpointing the ionized molecules from their mass-to-charge ratio. The TOF-MS method uses the fact that a charged molecule, after being accelerated in an electric field, will always travel a certain distance in a vacuum with a journey time proportional to its mass-to-charge ratio. In other words, lighter molecules travel faster than larger molecules with the same charge. For each and every molecule this travelling time acts as a fingerprint, which can be used to identify the contents of a sample.

The coffee-stain phenomenon enters the picture when the sample dries out. When the solvent

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**At a Glance: Coffee-stain effect**

- When a droplet of liquid dries on a surface, the volatile solvent (e.g. water) evaporates leaving the non-volatile solute (e.g. coffee grounds) behind in a ring shape
- The ring-shaped deposit forms because the droplet’s edge is “pinned” to the surface and solute molecules flow to the edge from the interior of the droplet
- Applying a varying voltage between the droplet and its substrate in a technique called electrowetting can effectively suppress this “coffee-stain effect”
- Evaporated droplets can then form small, concentrated, homogeneous spots instead of large, diffuse, heterogeneous rings
- This change allows a revolution in a workhorse molecular-analysis method at the heart of the life sciences, and also in circuit printing
By increasing and decreasing an applied voltage, the contact line is continuously kept in motion and is not allowed to pin a dielectric layer on which they sit. Electrowetting neither modifies the surface nor the liquid but solely changes their interaction. In essence, charge is added to the liquid either by redistributing existing charge, or by introducing charge through minute amounts of redox reactions.

Electrowetting is a bit like charging a capacitor, with the droplet being the electrode, the lower substrate being the counter electrode, and the upper substrate being a thin dielectric layer (see inset of figure 2). If a voltage is applied to the counter electrode, the droplet gains the same amount of charge but with the opposite sign. As a result, the two charges attract, and as the like charges inside the droplet repel each other, the droplet spreads out like a pancake, wetting the surface even more. When the voltage is removed, the induced charge disappears, allowing the droplet to return to its initial position. In short, electrowetting is a way of changing the position of the contact line of the droplet edge.

In 2011, working in the Physics of Complex Fluids Group at the University of Twente, we developed an electrowetting-based method that allowed us to suppress the coffee-stain effect so that a drying droplet instead forms a small, homogeneous residue (figure 2). By periodically increasing and decreasing an applied voltage to the counter electrode, the contact line is continuously kept in motion and is not allowed to pin. The result: one of the conditions for coffee-ring formation of the Deegan scenario is eliminated.

Furthermore, the changing voltage can create internal flow patterns within the droplet. Shaking the droplet at its mechanical resonance frequency or thereabouts causes particularly large amplitude oscillations. Eddies then form within the droplets in a nonlinear effect rather like the “Stokes drift” phenomenon that creates wavy patterns on a sandy beach. (The waves drag seawater over the beach floor, and where the moving water and sea floor meet create eddies that form patterns in the sand.) The driving waves in our experiments are the capillary waves, i.e. the movement of water as the droplet expands and contracts on the surface, and it is these waves that cause eddies. The result is that whenever a particle is pushed towards the contact line, it is then swept away again by the eddies. In other words, these flow fields counteract evaporation-driven net flow, the second of Deegan’s requirements. The most effective suppression is achieved when both conditions of coffee-ring formation are eliminated at the same time. Time-lapse photography showing a droplet drying using this method is shown in figure 3.
Stain gain
The electrowetting-based method for stopping coffee stains from forming has been successfully demonstrated in evaporating drops containing DNA and other biomolecules, and colloids ranging from 100 nm up to 5 µm. Combining this electrowetting method with MALDI-TOF-MS – a technique coined eMALDI – could give huge gains by reducing analysis times and enhancing the signal. The signal is improved because of the high concentration of molecules in the residue. The analysis time, on the other hand, is shortened by eliminating the time-consuming search for hot spots. The sample can be concentrated at a given position using the counter electrode, or, taking this further, a clever arrangement of counter electrodes can be used to position multiple samples in an array. In either case, the laser can then be aligned with the pre-known position and hit the sample first time.

The eMALDI technique, in other words, is a faster, more sensitive breed of MALDI-TOF-MS that in years to come could enable it to be used in clinical applications in hospitals and, from there, our daily lives. In recognition of the potential applications of eMALDI, our group at Twente recently won a subsidy from the Dutch Foundation of Technical Sciences (STW) to make a real device and bring this to market. If this effort is a success, then it could be time for analytical biologists and chemists to breathe a sigh of relief and say goodbye to coffee stains – at least in their samples, if not from their mugs.

More about: Coffee-stain effect
R D Deegan et al. 1997 Capillary flow as the cause of ring stains from dried liquid drops Nature 389 827
H B Eral et al. 2011 Suppressing the coffee stain effect: how to control colloidal self-assembly in evaporating drops using electrowetting Soft Matter 7 4954
F Mugele and J-C Baret 2005 Electrowetting: from basics to applications J. Phys.: Condens. Matter 17 R705
More information about eMALDI: www.emaldi.eu
Physics of Complex Fluids Group: www.utwente.nl/tnw/pcf
Short eMALDI film: www.youtube.com/watch?v=xwipCVZnN4E

Drink and think
Next time you spill some coffee, note how the suspended particles concentrate around the edge.