Surface Patterning

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Re-Shaping the Coffee Ring

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"coffee rings" · colloids · controlled evaporation · surface patterning

In 1997, Deegan, and co-workers[1] explained the commonly observed deposition of "coffee rings" of colloidal particles left behind after millimeter-sized water droplets resting on surfaces have dried out. They showed that a ring, rather than a uniform spot, is formed because the edge, or contact line, of such droplets is stuck or pinned, and water must therefore be drawn from the center to the edge to keep the contact line fixed as evaporation proceeds. This evaporation-driven flow drags suspended particles or solute towards the contact line, where it is deposited when the solvent evaporates there. It is remarkable that that this phenomenon of "coffee-ring" stains, seen every day on drying dishware, for example, was not explained until recently. But after this long neglect, there is now an explosion of recent research activity. The paper of Deegan et al. has been cited more than 1200 times, and has inspired numerous remarkable discoveries. Among the more surprising of these is the work published recently by Yunker et al.,[2] showing that if spherical colloids are replaced by even slightly elongated ones (with length to width aspect ratio of 1.2 or higher), the coffee ring disappears and is replaced by a much more uniform deposition! The transition from edge to uniform deposition is evidently induced by jamming of the monolayer of elongated particles at the surface of the droplet, and is influenced by the particle aspect ratio and the particle concentration. In mixtures of spheres and elongated spheres (which are called "spheroids"), jamming is also influenced by the ratio of sizes of the spheres and spheroids. Jamming at the droplet surface opens up a new method of controlling deposition patterns through change of solute shape and shape distribution. (Yunker et al. call their spheroids "ellipsoids," which is slightly imprecise terminology, since the term "ellipsoid" usually refers to particles whose three axes all differ in length, while "spheroids" are axisymmetric particles with two axes equal in length and the third longer than the other two, yielding a prolate shape in the case of the particles of Yunker et al.) It would be of interest also to examine surface-jamming transitions of flat, oblate, spheroidal particles, and of ellipsoidal particles whose three axes all differ in length. The transition is also likely influenced by particle surface changes, van der Waals interactions, surface roughness, particle–liquid contact angle, and other variables, opening up scope for a wide range of future studies and applications.

These "coffee-ring" and related stains are no mere curiosity, but involve a wide variety of phenomena at the forefront of scientific interest, including super-hydrophobicity,[3] contact-line motion, directed assembly,[4] thermal and solutal Marangoni flow,[5] flow instabilities, and formation of a surface-skin that can buckle into dimpled droplet shapes.[6] Practical applications of deposition from a drying droplet include inkjet printing,[7] DNA or RNA micro-array formation,[8] substrate patterning,[9] nano-material assembly,[4] and others.

The use of particle shape to regulate deposition patterns is the latest of a series of methods discovered for controlling deposition patterns. Other methods include the use of 1) thermal Marangoni flows, 2) solutal Marangoni flows, 3) control of contact-line motion, 4) patterned substrates, 5) solute crystallization, and 6) interfacial buckling.

Marangoni flows are produced by gradients of the surface tension along the surface of the droplet, which creates a shear stress that drags fluid along the interface, setting up recirculating flows.[5] These gradients of surface tension can be produced by temperature gradients along the droplet surface. Temperature changes arise from evaporation, which is non-uniform along the droplet surface because of both the non-uniform evaporation rate, and the non-uniform rates of heat transfer to the surface through the droplet. Both sources of non-uniformity are influenced by droplet shape, especially the ratio of droplet height to radius. Flat droplets yield faster evaporation at the droplet edge than the center. The rate of thermal conduction through the droplet and the underlying substrate also strongly influences surface temperature gradients. Depending on the balance of these two rates, thermal Marangoni convection can carry particles either towards the edge of the droplet or towards the center, thus providing a means of control of deposition patterns. This control was beautifully exploited by Harris et al.,[4a] who deployed a mask with a patterned array of holes above a drying droplet. This produced a patterned rate of evaporation on the droplet surface, which was reflected in similarly patterned deposition on the substrate; see Figure 1 a.

Gradients in surface tension can also be produced by gradients in concentration of solute along the droplet surface, which leads to solutal Marangoni flow, which can also be exploited to control deposition patterns. A striking example of this can be found in the work of Truskett and Stebe,[10] who deployed a surfactant monolayer on the water droplet surface

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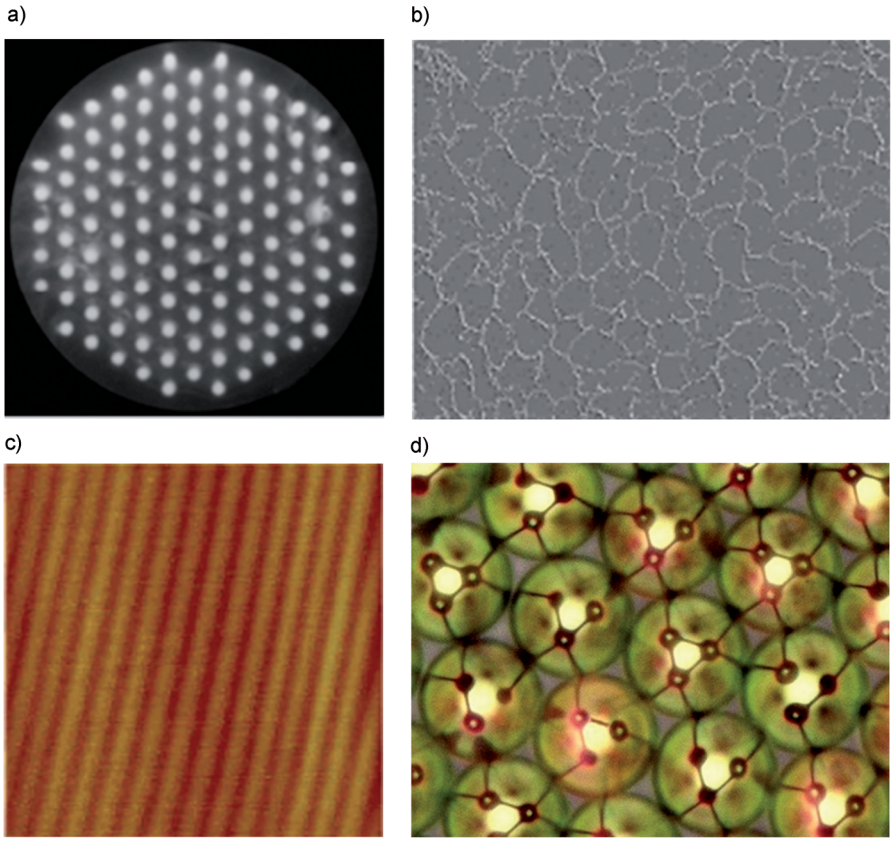

Figure 1. Control of deposition patterns from a drying droplet. In a) a mask with holes is placed above a drying droplet, leading to controlled thermal Marangoni flow patterns that produce geometrically similar colloidal particle patterns on an underlying substrate. Reproduced with permission from Ref. [4a]. In b) a surfactant spread on the surface of a drying droplet produces solutal Marangoni flow cells, leading to cellular deposition of colloids. Reproduced with permission from Ref.[10]. In c) periodic stick–slip contact line motion deposits rings of polymer solute. Reproduced with permission from Ref. [11]. In d) a pre-patterned particle array produces residual pendant rings after most liquid is dried. Completion of drying deposits lines of gold nanoparticles as a residue. Reproduced with permission from Ref. [9].

that undergoes a two-dimensional phase change (from "gas" to liquid expanded to liquid condensed) as surfactant concentration and drying conditions are varied. Such monolayers could both induce Marangoni flow and act to selectively block evaporation, depending on the surfactant phase state, thus affecting the deposition patterns of colloids suspended in the droplet; see Figure 1 b.

Contact-line motion can also generate patterns. This is of special interest if the contact line motion can be regulated through the depositions that occur at the contact line. Generally, these depositions pin the contact line, but this pinning can be overcome when the droplet flattens enough to reduce the contact angle below a critical de-pinning angle. Once mobilized, the contact line may retreat until the contact angle increases enough to re-pin the contact line. A repeat of this cycle leads to a sequence of concentric contact rings that can be very regular; see Figure 1 c.[11]

A fourth example of manipulating colloidal deposition is substrate patterning. A beautiful example of this is represented by the work of Vakarelski and co-workers,[9] who dried a droplet over a substrate pre-patterned with a regular array of polystyrene particles. Gold nanoparticles were added to the droplet liquid, which retreated into pendular rings around the polystyrene particles near the end of drying, and final evaporation of these rings deposited the gold nanoparticles into well-defined lines. The stability of the line-formation process was assisted by an added surfactant; see Figure 1 d.

A fifth method is through control of crystallization patterns during drying. For example, a wide variety of deposition patterns can be achieved through evaporation of water droplets containing proteins mixed with various salts.[12] Evaporation leads to super-saturation of salts, which crystallize in patterns that depend on the choice of protein, salt, and their concentrations, as well as the hydrophobicity of the substrate.

A sixth method of controlling deposition is through the formation of a solute crust on the surface of the droplet. the crust resists shrinkage and so eventually buckles under compressive stresses as the droplet shrinks because of evaporation. This kind of patterning was achieved by Kajiya, et al.,[6] who dried out polymer-containing liquid droplets, which produced solid polymer crusts at the free surface. These crusts buckled under continued evaporation, producing volcano-like polymer deposits once the solvent had been completely evaporated.

Thus, to the above methods of manipulating colloidal deposition from drying droplets, the new work of Yunker et al. thus adds a seventh, extremely novel, method, namely the exploitation of colloidal particle shape to control the deposition pattern, through jamming of particle surface layers. Not only is the method of Yunker et al. especially simple, it could be combined with other methods to produce additional novel phenomena and new deposition patterns. In addition, since the range of particle shapes and wettabilities is wide, and the possibilities for mixing particles of different shape and other properties is practically endless, the new results of Yunker et al. suggest that we are still far from discovering all the droplet deposition patterns that might be possible. Thus, more surprises no doubt await us in the rich field of particle and solute deposition from drying droplets.

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