



Controlled Uniform Coating from the Interplay of Marangoni Flows and Surface-Adsorbed Macromolecules

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Surface coatings and patterning technologies are essential for various physicochemical applications. In this Letter, we describe key parameters to achieve uniform particle coatings from binary solutions. First, multiple sequential Marangoni flows, set by solute and surfactant simultaneously, prevent nonuniform particle distributions and continuously mix suspended materials during droplet evaporation. Second, we show the importance of particle-surface interactions that can be established by surface-adsorbed macromolecules. To achieve a uniform deposit in a binary mixture, a small concentration of surfactant and surface-adsorbed polymer (0.05 wt% each) is sufficient, which offers a new physicochemical avenue for control of coatings.

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An evaporating liquid drop, either single or multi-component, containing solutes or particulates, leaves a deposit whose form is determined by various parameters, for instance, internal flow fields [1–3], liquid compositions [4–10], and interactions between suspended particles and a solid substrate [11–14], which are crucial for coating processes. In particular, control of the deposit uniformity and thickness can be important in surface patterning [15–17], ink-jet [4,18,19], and 3D printing technologies [20]. These processes are complex because of physicochemical dynamics that arise from Marangoni effects [2,5–10,12,21,22] and particle deposition mechanisms [11,12,14,23]. In fact, although a binary mixture is used quite often to achieve uniform particle deposition from droplets smaller than 100 μm [4,18,19], to our best knowledge such coatings have not been achieved for larger droplets. Furthermore, while the wetting and dewetting behaviors of binary mixture drops have been investigated [24,25], the relation between the deposition pattern and the evaporatively driven flow field in a binary mixture droplet is incomplete (Table S1, in the Supplemental Material [26]).

In this Letter, to achieve a uniform coating, we identify key characteristics of a multicomponent solution, which consists of a binary mixture, surface-active surfactant, and surface-adsorbed polymer. We were motivated to pursue the ideas here from examining a whisky droplet after drying on an ordinary glass where it creates a relatively uniform particle deposit (see Fig. 1), which is in contrast to the well-known “coffee-ring stain” [1]. Based on our understanding of the drying and coating mechanisms of binary liquid droplets, whisky droplets, and more complex solution droplets, we design a model liquid that yields nearly uniform deposits by taking the approach that whisky is an ethanol-water mixture containing diverse dissolved molecules, which contribute to the complexity of the system, the flows, and the final particle deposits.

We begin with a few remarks about whisky, since it serves as a model complex mixture, where nearly uniform particle deposits are observed after drying. Whisky is an alcoholic liquid (ethanol:water, 35:65% by weight) made by the hydrolytic breakdown of cereal starches into fermentable sugars and their subsequent fermentation and distillation [40]; see the Supplemental Material [26] for a brief summary. During the manufacturing procedures, various chemicals are formed, e.g., cellulose, hemicellulose, lignin, and a number of highly extractable molecules, including lipids, acids, sugars, and tannins [41]. However, their volume fractions are smaller than 1% in total [40].

We investigated the flow field inside an evaporating whisky drop by using particle image velocimetry (PIV) and recorded images of the final particle deposits (Movie 1 in Ref. [26]). To visualize the flow field inside droplets, we added 1 μm diameter fluorescent particles (carboxylate-modified polystyrene, Invitrogen, USA) at a concentration of 8×10^{-4} vol%. A liquid volume $0.60 \pm 0.07 \mu\text{l}$ was deposited on top of a solid substrate (VWR, USA) (see

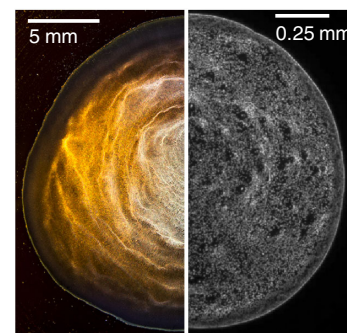


FIG. 1. Left: A dried mark of a whisky droplet (Macallan, UK) on a normal glass. The image is obtained using an orange color flashlight. Right: A dried deposit pattern of a Glenlivet whisky (UK) with fluorescent polystyrene particles.

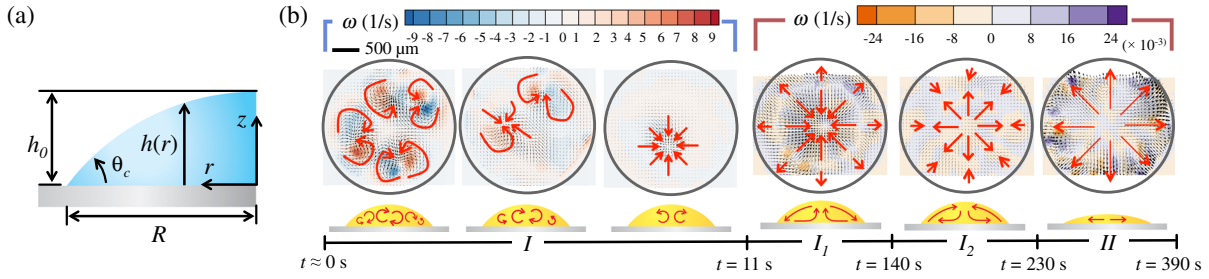


FIG. 2. (a) Sketch of a liquid drop on a solid substrate. (b) Flow fields (vectors) and wall-normal vorticity ω fields (color contours) of a Glenlivet whisky. The flow field was measured near the substrate. The total drying time was about 470 s. Below each flow field plot a schematic of the side view of the evaporating droplet is provided. The red arrows represent the flow pattern. There are different flow regimes, multiple vortices (I), two circulatory flows (I_1 and I_2), and radial outward flow (II). At the stage II , from the outward radial flow, we estimate that the ethanol is almost evaporated and there is no significant surfactant effect along the droplet interface.

experimental details, Fig. S1 and Sec. S2, Supplemental Material [26]). During evaporation, the temperature and relative humidity were fixed, i.e., $T = 299$ K and $RH = 50\%$. The whisky drop (Glenlivet, UK) initially has radius $R = 1.3$ mm, height $h_0 = 0.46$ mm, and apparent contact angle $\theta_c = 36^\circ$ [see notations in Fig. 2(a)].

Initially (regime I), multiple vortices are observed as shown in Fig. 2(b), which is similar to the flow pattern of an ethanol-water (35:65 wt%) mixture [Fig. S2(a), Ref. [26]]. The complicated mixing flows are driven by solutal-Marangoni effects caused by a concentration variation because of the evaporation of ethanol [5,6]. Because of this Marangoni flow, the particles are distributed everywhere. The typical flow speed is $U = \mathcal{O}(100 \mu\text{m/s})$ and the wall-normal vorticity is $\omega = [(\partial u_y / \partial x) - (\partial u_x / \partial y)] = \mathcal{O}(1 \text{ s}^{-1})$ for in-plane velocity (u_x, u_y) .

After regime I , the flow is directed radially outward along the air-liquid interface and radially inward along the substrate [see the schematic side view of regime I_1 of Fig. 2(b)]. The flow speed is $U = \mathcal{O}(1 \mu\text{m/s})$ and the vorticity becomes weaker compared to regime I , e.g., $\omega = \mathcal{O}(10^{-3} \text{ s}^{-1})$, as the size and strength of the vortex change. As the whisky drop evaporates further, we observed a reversed flow pattern showing an outward radial flow along the substrate and an inward radial flow along the air-liquid interface [regime I_2 of Fig. 2(b)]. Next, an outward capillary flow is observed as shown in regime II of Fig. 2(b) [1]. Thus, by this time we can assume that ethanol is almost completely evaporated. The distinct particle deposits after whisky completely dries appear linked to the flow fields identified as regimes I_1 and I_2 , which are not observed in the ethanol-water (35:65 wt%) mixture droplet (Movie 2 in Ref. [26]). Therefore, an ethanol-water mixture cannot produce a uniform deposit [Fig. S2(b), Ref. [26]].

From the flow field differences between the whisky drop and the ethanol-water mixture drop, we suspect that some chemical compounds play a role in this flow field. To check, we completely dried the whisky at room temperature ($T = 298$ K) and the dried solid residue of whisky was

resolubilized in deionized water. Then, we investigated the flow field of this mixture droplet during evaporation. We observed that particles accumulated at the contact line were released from the contact line and moved along the liquid-air interface to the top center of the droplet due to a surfactant-driven Marangoni effect [42] (Movie 3 in Ref. [26]). We measured the surface tension of this solution to be 60.5 mN/m, which is lower than distilled water's surface tension 72.0 mN/m, and so we conclude that whisky contains molecules acting as surfactants. Natural phospholipids from various grains of whisky's raw materials including barley, wheat, corn, and rye have been detected in whisky and, are the most likely source of these natural surfactants (Sec. S1, Ref. [26]).

To check the effect of the surfactant, we prepared an ethanol-water (35:65 wt%) mixture containing 0.05 wt% sodium dodecyl sulfate (SDS, Sigma-Aldrich, USA), and we recorded the flow field and dried pattern. SDS is a common surfactant that has been used in previous studies of Marangoni flows [8,12,42]. In our system, the initial surfactant concentration is lower than the critical micelle concentration [43]. By adding surfactants, we mimicked the flow pattern of a drying whisky drop [Figs. 2(b) and 3(a)]: two different circulating flows are observed after the initial multiple vortical flows. As the droplet evaporates, the ethanol concentration near the contact line is lower than that of the drop center due to the nonuniform evaporative flux along the droplet height [6], so the solutal Marangoni stress occurs along the droplet interface [Fig. 3(b)]. Simultaneously, as the surface-active molecules, which in this case are a dissolved surfactant, accumulate at the contact line [8] and the ethanol concentration decreases in time, the surfactant-driven Marangoni stress becomes dominant [Fig. 3(c)]. This flow transition indicates that initially a solutal Marangoni effect is dominant compared to a surfactant-driven Marangoni effect. From this and based on the literature [6,7,42], in this problem we can establish the hierarchy of Marangoni effects, i.e., (i) solutal, (ii) surfactant, and (iii) the thermal Marangoni effect. As a consequence of this competition between solutal- and

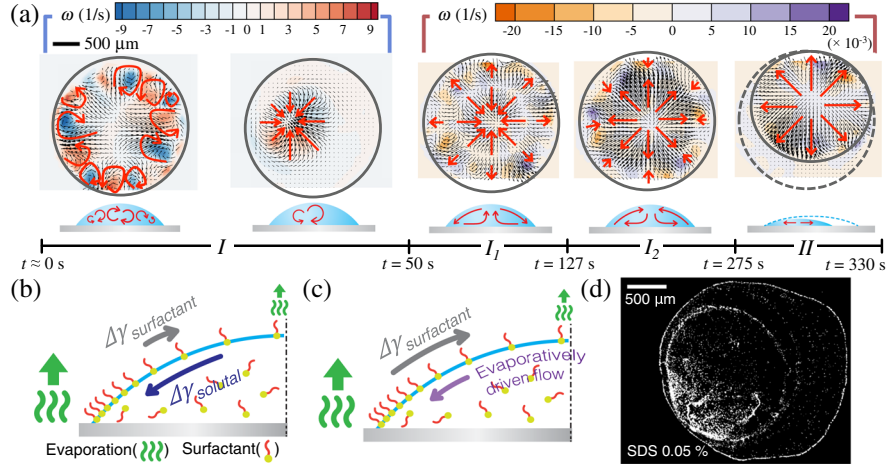


FIG. 3. (a) Flow fields (vectors) and wall-normal vorticity ω fields (color contours) of an ethanol-water (35:65 wt%) mixture with 0.05 wt% SDS. Below each flow field plot a schematic of the side view of the evaporating droplet is provided. The red arrows represent the flow pattern. The total drying time was about 400 s. At the stage *II*, from the outward radial flow, we estimate that the ethanol is almost evaporated and there is no significant surfactant effect along the droplet interface. Schematic of (b) solutal and surfactant-driven Marangoni effects and (c) the surfactant-driven Marangoni effect and the evaporatively driven flow effect along the drop interface. The gray, dark blue, and light purple arrows indicate the surfactant, solutal, and evaporative flux effects, respectively. (d) The final deposition pattern of the binary mixture drop with SDS on the cover glass where the particle concentration is 8×10^{-4} vol%.

surfactant-driven Marangoni stresses, we observe the sequence of opposite signed circulatory flows. The critical temporal evolution of the circulation transition can be investigated further by studying the droplet shape or the concentration of solute and surfactant. At longer times, if the surfactant is saturated everywhere, a typical outward radial capillary flow is observed [regime *II*, Figs. 2(b) and 3(a)].

The critical condition to induce the Marangoni flow caused by a surfactant and/or solute is considered next. The ethanol-water droplet with SDS is thin because $h_0/R < 1$ where $h_0 \approx 100 \mu\text{m}$ and $R \approx 1 \text{mm}$ for late times (e.g., after regime *I*). The typical flow speed $U \approx 1 \mu\text{m/s}$ (from PIV results), so that the Reynolds number $\text{Re} = \rho U h_0 / \mu \approx 10^{-4}$, where density $\rho \approx 10^3 \text{kg/m}^3$ and viscosity $\mu \approx 1 \text{mPa}\cdot\text{s}$. Furthermore, the surface tension force is dominant compared to both the viscous and gravity forces, as the capillary number $\text{Ca} = \mu U / \gamma \approx 10^{-7}$ and the Bond number $\text{Bo} = \rho g R^2 / \gamma \approx 10^{-1}$, where $g = 9.8 \text{m/s}^2$ is gravity and $\gamma \approx 72 \text{mN/m}$ is the surface tension of water. Therefore, by using the lubrication approximation, in cylindrical (r, z) coordinates the Navier-Stokes equations can be simplified and the surface velocity $u(r, t)$ at the liquid-air interface $z = h(r, t)$, nearly, a spherical cap, can be expressed as (see details in Sec. S4, of the Supplemental Material [26])

$$u(r, t) = \underbrace{\frac{\gamma h^2}{2\mu} \left(\frac{\partial p}{\partial r} \right)}_{\text{capillary effect}} + \underbrace{\frac{h}{\mu} \frac{\partial \gamma}{\partial r}}_{\text{Marangoni effect}} \quad \text{at } z = h(r, t). \quad (1)$$

Here, the capillary pressure $p = -\gamma \nabla^2 \tilde{h}$, where $\tilde{h} (\ll h_0)$ is the perturbation to the liquid-air interface caused by the internal flow. Then, the interfacial velocity driven by the capillary pressure gradient scales as $(\gamma h_0^2 \tilde{h}) / (\mu R^3)$ and the interfacial velocity driven by Marangoni effects is expected to have a magnitude of $(h_0 \Delta\gamma) / (\mu R)$ where the sign of $\Delta\gamma$ determines the flow direction. If both velocities have the same order of magnitude,

$$\left| \frac{\Delta\gamma}{\gamma} \frac{R^2}{h_0 \tilde{h}} \right| \approx 1, \quad (2)$$

then, for large interface deformation $\tilde{h} \rightarrow h_0$, we obtain the upper bound for $|\Delta\gamma|$ of about 1 mN/m. This value is consistent with previous studies on the interface deformation of an evaporating droplet by Marangoni effects [10,44]. On the other hand, experimental observations indicate $|\Delta\gamma| \approx 1 \mu\text{N/m}$, for an evaporating water drop with SDS, which maintains a nearly spherical cap shape [42]. From Eq. (2), we estimate $\tilde{h} \sim 0.1 \mu\text{m}$, which is negligible compared to the droplet size.

Although we mimicked the flow pattern of the drying of a whisky drop by adding SDS to a binary mixture, the particles are not uniformly distributed on the substrate, as shown in Fig. 3(d). We observed that in the model liquid drop when the contact line recedes, the contact line transports particles towards the center of the drop [Movie 4 in Ref. [26]] [12,45]. However, for a whisky drop, although the contact line recedes, the particles remain nearly uniformly distributed on a substrate [Movie 1 in Ref. [26]].

The chemical composition of whisky has been extensively investigated. According to the literature (see Sec. S1

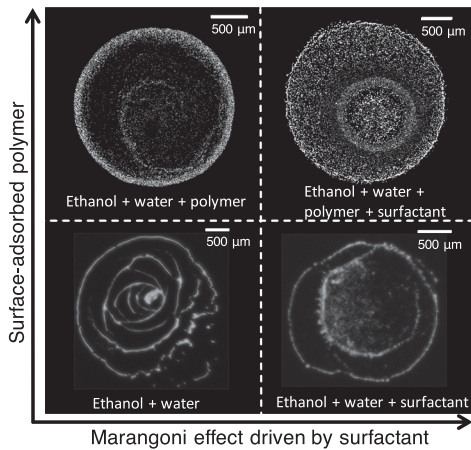


FIG. 4. A diagram of effects of surfactant driven Marangoni flows and surface-adsorbed materials in the binary mixture on the final deposit. The concentration of ethanol 35% in DI water. PEO (4×10^6 Da) and SDS concentration are 0.05 wt%, respectively.

of the Supplemental Material [26]), whisky contains natural polymers (e.g., lignin and polysaccharides). We hypothesize that some macromolecules, originally present in whisky, adsorb on a substrate and may play a role in adhesion and retention of the particles on the substrate. To test this idea, we added polymer, polyethylene oxide (PEO) (0.05 wt%), to the ethanol-water mixture with surfactant (0.05 wt%). At this polymer concentration, the polymer does not influence the flow field until regime I_2 . When the contact line recedes (regime II), the added polymer contributes to capture the particles on the surface but without polymers the receding contact line transports particles (see Movies 4 and 5 in Ref. [26]).

It is known that PEO can adsorb onto silica [46–48] creating a “pseudobrush” structure on the glass surface. The spatial density of the adsorbed polymer is about 1 mg/m^2 [49], such that the quantity of adsorbed polymer is extremely small compared to the suspended polymer. As evaporation proceeds, the polymer concentration in the droplet increases. The polymer adheres on the silica substrate, which is not transported by the receding contact line. As a result, the particles are captured by a dense polymer structure and then remain adhered on the substrate. This adherence mechanism can be reproduced with different molecular weights (2×10^4 – 4×10^6 Da, PEO) and other polymers, e.g., hydroxyethylcellulose, polyvinyl alcohol, and polyvinylpyrrolidone (Fig. S3, Supplemental Material [26]).

Also, we tested the effect of polymer without surfactant and a primary ring pattern is observed along the contact line (see Fig. 4), which is the signature of the coffee-ring effect. As a result, the surfactant is crucial to prevent particle accumulation along the contact line.

In Fig. 5(a), we compare the final deposition pattern of whisky, water, and the model liquid (respectively, from left

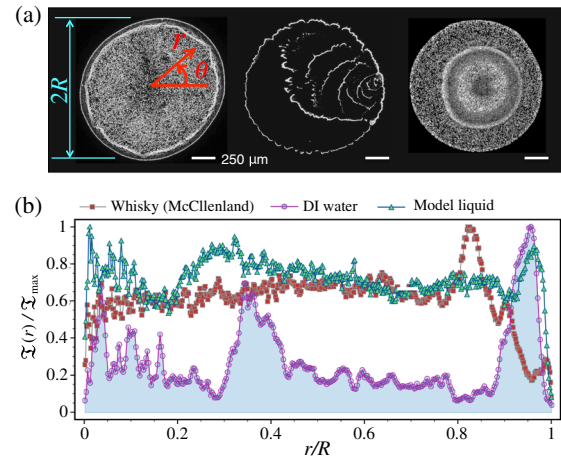


FIG. 5. (a) Comparison of the final deposition patterns on top of the cover glass (VWR, USA): (left) whisky (McClennland, UK), (center) water, and (right) a model liquid [ethanol:water (35%:65%) + SDS(0.05%) + PEO(0.05%) by weight] containing $1 \mu\text{m}$ polystyrene particles (5×10^{-3} vol%). $2R$ is the diameter of the final area. (b) Deposit profiles along r are plotted for each of the images in (a). The intensity profile $\Xi(r)$ is normalized with the maximum of $\Xi(r)$ where $\Xi(r) = (1/2\pi) \int_0^{2\pi} i(r, \theta) d\theta$ and $i(r, \theta)$ is the local light intensity.

to right), which are deposited on top of a cover glass. We then measure the average particle number density as a function of radial location [Fig. 5(b)], which exhibits significant correspondence in coating uniformity between whisky and the model liquid. As shown in Fig. 5, the proposed model liquid can produce a nearly uniform deposit. Here, we should note that different types of polymers can create different patterns [Figs. S3(b)–3(f), Supplemental Material [26]). Presumably, the surface adsorbed macromolecules in whisky are not identical with the polymers that we used in this study. We also obtained a nearly uniform particle deposition pattern with another glass substrate, which has a lower contact angle with water (Fig. S4, Ref. [26]).

In this Letter, we have shown that a combination of a binary mixture, surfactant, and surface-adsorbed polymer influences the final deposition pattern so that more uniform deposits occur. Based on an understanding of the drying and coating mechanisms, we demonstrate that continuous mixing by distinct Marangoni flows and strong interaction between particles and a substrate are important to obtain a uniform deposit. Although the complex chemistry of whisky is not fully understood, we believe that these observations inspired by whisky drying are useful and applicable to coating processes more generally and the proposed method offers a new physicochemical avenue for control of coatings. To accomplish more controlled coatings, a future study can be devoted to analyze the interplay between the flow characteristics and the microstructure of a final deposit with respect to the spatial [1] and temporal [50] variations.

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