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Stains from Freeze-Dried Drops
Etienne Jambon-Puillet*

Institute of Physics, Van der Waals-Zeeman Institute, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands

Supporting Information

ABSTRACT: The evaporation of droplets of colloidal suspensions onto a surface is a common tool to achieve surface coatings and self-assembly. However, because of the spontaneous flow developing within an evaporating drop, the deposit is difficult to control, and an unwanted ring-like structure often forms, with particles aggregating along the drop edge. Here, by freezing the drops before sublimating them in dry air we propose a new approach that produces a different kind of stain where most particles are clustered in the center of the drops instead. We demonstrate that these deposits can be continuously tuned from wide but thin to concentrated and thick by varying the droplet’s aspect ratio.

Unlike evaporated liquid drops, stains from freeze-dried drops do not depend on the drying conditions or substrate roughness and possess a porous and branched microstructure somewhat reminiscent of freeze-casted ceramics. With these stains being governed by the freezing process rather than the drying, this opens alternative ways to control colloidal deposits.

INTRODUCTION
Spilled coffee, tea, or red wine left to dry usually leaves a stain that is darkest around its edge. This so-called coffee ring (Figure 1b) forms when a sessile drop containing nonvolatile solutes evaporates with a pinned contact line, a situation encountered on most substrates.1,2 In these circumstances, a capillary flow transporting the solute develops toward the drop edge to compensate for the stronger evaporation there.3−4 Since drying drops are used in many applications such as coating,5 printing,6 self-assembly,8,9 and biomedical assays,10,11 achieving a good understanding and control of the deposit formation is an important challenge. As a result, intense research efforts to understand and control the deposits left by dried liquid drops have yielded many innovative strategies, which all have limitations (see recent reviews on drop evaporation and deposition patterns12−16).

We present here a new approach in which we freeze drops of aqueous colloidal suspensions by cooling the substrate and then sublimate them in dry air, while frozen. In contrast with common coffee stains obtained from dried liquid drops, this approach yields a deposit in which most particles are concentrated in the center (Figure 1a). We systematically varied the drop volume as well as the substrate wettability, temperature, and roughness and show that, within these parameters, the stain solely and nonlinearly depends on the initial drop aspect ratio; the strength of the particle accumulation can be tuned to produce stains whose aspect ratio varies over several orders of magnitude. Electron microscopy images further reveal a porous and branched microstructure different from the compact deposits obtained from evaporated liquid drops9,17 and closer to freeze-casted ceramics18,19 where the particles are repelled by the solidification front.20−27 The clustering we observe in our stains is in fact caused by the transport of the particles toward the apex of the drop as the freezing front propagates upward. The stains from freeze-dried drops are therefore sensitive to parameters governing the freezing front—particle interaction rather than those determining the common coffee-stain type of deposits.

Figure 1. Stains left by drops dried while frozen (a) or liquid (supercooled) (b) under identical experimental conditions: droplet volume V ≈ 1 μL, glass substrate at T_s = −5 °C, relative humidity RH = 5%. Scale bar 0.5 mm.
for long periods of time, we the suspension are then deposited. As our drops remain supercooled quickly as the Peltier

Parylene-C (SCS Labcoter PDS 2010, additional coating thickness wettability (18° < θ < 103°). To test the influence of surface roughness, we sand plain glass cover slips (arithmetical mean deviation Sₐ ≈ 0.5 μm).

Sublimation Experiment. The experiment is conducted in an acrylic box (0.4 × 0.5 × 0.7 m³) where the relative humidity RH (with respect to the ambient air at T₀ = 24 °C) is monitored with a thermo-hygrometer Testo 645 (accuracy ±2%) and kept constant at a value low enough to sublimate our coldest drops (~5%) by gently blowing dry nitrogen. The physically relevant relative humidity at the frozen drop’s surface RHₕ is much higher and varies with the substrate temperature Tₑ, RHₕ = RHₚₑ(ψₑ(Tₑ))/RHₚₑ(T₀) where the saturation pressures over ice and water are calculated from eqs 7 and 10 of ref 28. The water vapor concentrations are then calculated from the ideal gas law; the water–air diffusion coefficient D(Tₑ) is calculated with the equation in Figure 78 of ref 29, and the ice density is taken as ρₑ = 918.9 kg m⁻³.

The cover slips are attached to a water-cooled Peltier system (Anton Paar TKE 150P-C) with thermal grease. Drops of 1~50 μL of the suspension are then deposited. As our drops remain supercooled for long periods of time, we first set the Peltier’s target temperature to its minimal value, therefore decreasing the substrate temperature as quickly as the Peltier’s feedback controller permits it until the drop freezes (∼-18 °C on rough glass and ∼-23 °C for the smooth substrates at a rate ∼1 °C/min). Then we set the Peltier to the desired sublimation temperature (reached in less than 10 s), between -2 °C and -15 °C.

The sublimation process is followed by means of side-view images recorded with a Nikon D5600 camera mounted with a high-magnification objective (Navitar). The images are analyzed using ImageJ and Matlab; drop volumes are measured by numerically integrating their profile (assuming axisymmetry) and their contact angle with the tangent method.

Figure 2. (a) Sequence of images showing the evaporation of the frozen drop whose stain is shown in Figure 1a. The images include the reflection of the drop on the substrate. The white dashed curve is the initial liquid drop profile, scale bar 1 mm. (b) Radius R (red circles) and height H (blue squares) of the same drop as a function of time t. The dashed and solid curves are the spheroid evaporation model: eq 1 with t₀ = 30 min and β = 7 × 10⁻¹¹ m² s⁻¹.

thus offering a new approach to control nonvolatile solute deposition.

EXPERIMENTAL SECTION

Materials. The aqueous suspension is prepared by diluting monodisperse polystyrene particles (Polybead microspheres from Polysciences, Inc.) of diameter 465 ± 11 nm in Milli-Q water (Millipore) at 0.08 wt % (volume fraction ϕ = 8 × 10⁻⁴). Although nonfunctionalized, the particles contain a slight anionic charge and traces of surfactant (the suspension and pure water have similar contact angles). Our substrates are thin glass cover slips (Menzel-Gläser #1, thickness 0.13~0.16 mm) either raw or coated with Parylene-C (SCS Labcoter PDS 2010, additional coating thickness ~1 μm). We further plasma treat both of the surfaces (Diener Zepto) and use them at various degrees of aging to continuously vary the wettability (18° < θ < 103°). To test the influence of surface roughness, we sand plain glass cover slips (arithmetical mean deviation Sₐ ≈ 0.5 μm).

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Stain Analysis. Once the ice droplets have completely dried, we remove the stains from the climatic chamber and use a 3D laser scanning confocal microscope (Keyence VK-X1000) to acquire both microscopy images (focus stacked, coaxial illumination) and height maps of the stains. Because the surfaces are quite irregular due to their microstructure, we fit them with 2D Gaussians in Matlab to quantify the global stain shape (see Figure 4a). The deposit average height h is extracted from the Gaussian amplitude while its radius r is the sum of the standard deviations in the principal directions. The stains are then coated with chromium or titanium (thickness ~20 nm) and imaged with a high-resolution scanning electron microscope (FEI Verios 460) to observe their microstructure.

RESULTS AND DISCUSSION

As for most suspension–substrate combinations, drying liquid drops of our suspension, either at room temperature or supercooled below the melting point as in Figure 1b, always leaves a pronounced coffee rings. This confirms that the contact line pins and that thermal and solutal Marangoni flows that could arise due to the small amount of surfactants in solution are negligible. Moreover, since both the particles and our substrates are slightly negatively charged, the DLVO interactions are repulsive and particles do not deposit on the substrate to form a uniform film. Instead, they are rapidly advected by the capillary flow at the drop edge and form a crystalline packing. Finally, the presence of the ring shows that the particle does not accumulate at the liquid–air interface as it would also result in a more uniform deposit.

Now turning to the drops that dried while frozen, snapshots of a typical experiment are shown in Figure 2a. Once frozen, a sharp tip develops on top of the drop due to the expansion of water upon freezing. The frozen drop then sublimates at a rate similar to that of liquid water evaporating under the same conditions. It first loses its sharp regions (tip and edges) to reach a spheroidal shape after roughly half of the total evaporation time (see Figure 2a, t = 42 min). This shape is then maintained until the end of the drying process. As the contact line retracts, particles at the drop edge are gradually deposited onto the substrate. It seems that, as the ice sublimates, particles are released on the drop surface and move along with it until they touch the substrate (see Movie S1 and Movie S2).

We first look at the drying dynamics in Figure 2b where we plot the height H and contact radius R of the drop as it...
sublimates. Except at the beginning of drying where the drop is still pointy, both parameters scale as $R(t) \sim H(t) \sim (t_f - t)^{1/2}$ with $t_f$ the total drying time. This behavior is similar to that of liquid drops evaporating with a constant contact angle. However, unlike liquid drops, the dynamics after the drop becomes spheroidal (for $t > t_0$ with $t_0 \approx t_f/2$ the smoothing time or equivalently $\hat{t} \equiv t - t_0 > 0$) can be described by a closed-form equation. We derive this equation by modeling the diffusion-limited sublimation of self-similar spheroids:

$$R(\hat{t}) = \sqrt{R_0^2 - 2\beta(C_0/H_0)\hat{t}}$$

$$H(\hat{t}) = (H_0/R_0)R(\hat{t})$$

Here, $C$ is the electrostatic capacitance:

$$C = \begin{cases} 
\sqrt{R^2 - H^2}/\arcsin(\sqrt{1 - (H/R)^2}) & \text{if } R > H \\
2\sqrt{H^2 - R^2}/\ln\left(\frac{H + \sqrt{H^2 - R^2}}{H - \sqrt{H^2 - R^2}}\right) & \text{if } R < H
\end{cases}$$

and the subscript “0” denotes the value at $\hat{t} = 0$ (i.e., $t = t_0$). In eq 1, all thermodynamic quantities are enclosed within $\beta = D(\rho_{\text{sat}} - \rho_{\infty})/\rho_{\text{ice}}$ with $D$ being the water diffusion coefficient, $\rho_{\text{sat}}$ the vapor saturation concentration over ice, $\rho_{\infty}$ the vapor concentration at infinity, and $\rho_{\text{ice}}$ the ice density. We plot eq 1 along with the experimental data in Figure 2b and find a very good agreement with $\beta$ fitted within the experimental uncertainties (error margin of 20% resulting from the humidity probe accuracy).

We now turn to the stains. We find that different substrate temperatures result in different drying speeds: drops at $-15^\circ$C take about 10 times longer to evaporate than drops at $-2^\circ$C, as expected from the model since $\beta$ is reduced by roughly a factor 10 and $t_f \sim 1/\beta$. However, we find that the final stains are very similar (see Supporting Information), indicating that the deposit is insensitive to the sublimation rate. This provides the opportunity to perform the drying step at enhanced sublimation rates using a partial vacuum and a condenser as in freeze-drying applications ($t_f \sim 1/\beta \sim 1/D \sim P$, with $P$ the pressure). In stark contrast, changing the substrate wettability dramatically alters the stain. Figure 3a–c shows three stains left

**Figure 3.** Effect of wettability on the stains [(a, d, g) glass, (b, e, h) plasma parylene, (c, f, i) parylene, $V \approx 5 \mu L$]. (a–c) Backlit side-view pictures of the final stain with the initial liquid drop profile (white dashed line). The images include the reflection on the substrate. Scale bars: 1 mm. (d–f) Microscopy images of the stains. (g–i) Height maps of the stains (in $\mu m$) color coded between 0 and the maximum height on each image.
by frozen drops, each with a volume of 5 μL, on substrates of increasing hydrophobicity (see also Movie S1 and Movie S2). The stain of the low contact angle drop is relatively thin and looks uniform from the side while the ones resulting from the drops with a higher contact angle leave a macroscopic spot-like residue in the center of the stain. Figure 3d-f shows the same stains seen from above with an optical microscope. We observe an outer region of varying size with a very thin layer of particles (dark gray) and a thicker central core (white). Gradually decreasing the wettability results in the particles increasingly accumulating in the core which becomes more confined and thicker. The thin outer region’s size concurrently decreases but with a lot more variability. To quantify this behavior we use a profilometer to measure the stain topography (see Figure 3g–i). While the outer region is always only a few particles high, the core region evolves from a collection of separated towers of a few tenths of microns at very low contact angles to a more compact half millimeter high spot at larger contact angles. Increasing the drop volume increases the stain size as one would expect from mass conservation, but it also modifies its aspect ratio at large volumes, when the drop starts to get flattened by gravity (see Supporting Information). This suggests that it is not the substrate wettability θ which dictates the strength of particle clustering in the core but the drop aspect ratio $H/R$. Finally, since the substrate roughness influences the pinning for liquid drops and in return their stains, we sand glass cover slips to check roughness effects on our freeze-dried drops. No pinning of the ice contact line is observed, and the stains are similar to the one sublimated on smooth substrates (at constant drop aspect ratio) suggesting that the roughness does not induce specific particle–substrate interactions.

To characterize the aggregation of particles in the core of the stain, we fit the height maps with 2D Gaussians as shown in Figure 4a. We then extract the core average height $h$ and radius $r$ from the fits (see Experimental Section). Aggregating all our data for drops of different volumes on different substrates sublimated at different temperatures, we plot the core aspect ratio $h/r$ as a function of the drop aspect ratio $H/R$ in Figure 4b. The data fall on a single master curve indicating that the
stain shape solely depends on the initial drop shape. Plotting the same data on a log−log scale (see inset Figure 4b) reveals a power law dependence $h/r = a(H/R)^\alpha$ that we fit to get $a = 0.55$ and $\alpha = 4.0$. We can then couple this empirical fit to mass conservation to disentangle the height $h$ and radius $r$. Since the stains are reasonably Gaussian, their volume is roughly $\pi hr^2/2$. Conservation of the particles therefore gives $\phi \pi hr^2/2 \approx \phi V$ with $\phi$ the average stain packing fraction. If this packing fraction is constant throughout our experiments, then by using $h/r = a(H/R)^\alpha$ we expect the following power laws for the dimensionless stain height and radius:

$$\frac{h}{V^{1/3}} = a^{2/3} \left( \frac{2\phi}{\pi \phi} \right)^{1/3} \left( \frac{H}{R} \right)^{2a/3}$$

$$\frac{r}{V^{1/3}} = a^{-1/3} \left( \frac{2\phi}{\pi \phi} \right)^{1/3} \left( \frac{H}{R} \right)^{-\alpha/3}$$  \hspace{1cm} (3)

Since we know $a$ and $\alpha$ from the initial fit, only the average stain packing fraction $\phi$ is unknown, and it can be extracted from the prefactors.

We plot the dimensionless stain radius in Figure 4c and height in Figure 4d as a function of the drop aspect ratio. The data collapse on power laws with the exponents given by eqs 3,4, thus confirming that our stains have a reasonably constant porosity. We then simply fit their prefactor and get an average stain packing fraction of $\phi = 0.19 \pm 0.07$, showing that our stains are quite porous, much more than typical coffee rings or ball-like deposits obtained with a depinning strategy\textsuperscript{(39,40)} (for which $\phi \sim 0.4$−0.7). We investigate this particular porous microstructure with electron microscopy. Figure 5a shows an overview of a representative stain. The spot-like core where most of the particles accumulate is very distinguishable from the outer region. The outer region consists of concentric stripes of small aggregates which become smaller and more isotropic as we move away from the core, toward the stain edge. The core itself consists of a rather compact central spot with a more porous edge with concentric voids much larger than the particles. The core’s edge (Figure 5b) consists of clumps of particles aggregated together to form an interconnected network with large holes (black regions). The core’s center (Figure 5c) contains the same kind of clumps but stacked together in a more compact way. Details of the clumps themselves are shown in Figure 5d: they are compact with a short-range hexagonal order. The stain’s porosity therefore comes from the irregular clustering of the clumps.

Finally, we discuss the physical mechanism responsible for the particular structure of our frozen stains. The particles cannot be homogeneously distributed within the frozen drop and simply deposited on the surface below during sublimation. If that was the case, we would expect stains with an aspect ratio roughly equal to the drop aspect ratio itself and not the very nonlinear dependence observed in Figure 4b. As the ice sublimates, particles are released on top of the drop surface and more or less follow the interface until they reach the substrate (see Movie S1 and Movie S2). It is well-known that liquid

Figure 5. Electron microscopy images of the stain in Figure 3b,e,h which has an intermediate aspect ratio: $h = 66.5$ μm, $r = 469$ μm. (a) Overview of the stain. (b) Close-up view of the edge of the core region. (c, d) Close-up views of the center of the core.
interfaces can capture particles, transport them, and self-assemble them in various structures (e.g., ref 8). Here, analogously, by preventing the particles from rolling off from the curved solid surface through adhesion and/or friction, this interfacial capture constitutes a first mechanism to cause central aggregation. However, this mechanism is not very strong since thin drops still produce thin stains, and this would not explain the particular microstructure observed as we would rather expect an homogeneous stain with particles in random loose packing. Another mechanism must therefore be responsible for the clustering and microstructure observed.

As solidification fronts propagate, they exert thermomolecular forces on impurities suspended in the melt. Depending on the front velocity $v$, a particle is either repelled by the front or engulfed. $^{23,25}$ Although models exist for the case of individual particles, $^{23-25}$ the behavior of suspensions where particles interact with each other is still unclear. $^{26,27,41}$ Various engulfment patterns have been observed with particles aggregated in bands parallel to planar fronts, $^{41}$ between dendrites, or at grain boundaries. $^{42}$ In past decades, this particle–front interaction has been used to produce highly anisotropic porous structures after drying/dissolving the solidified matrix, a technique now called freeze-casting. $^{8,19,43}$

These freeze-casted structures, although much more regular and anisotropic, share some similarities with the microstructure of our stains. The differences probably come from the absence of binders in our drops to hold the particles in place, and therefore, part of the structure collapses on itself during the drying and is perhaps transported on the receding interface. These similarities strongly suggest that here, also, the particle–front interaction is responsible for the stain microstructure.

Consequently, we now focus on the freezing process. Because our drops are supercooled, they freeze in two stages (see Movie S3). They first go through a recrystallization stage where a very fast front ($v \approx 0.2 \text{ m/s}$) propagates on the whole droplet and freezes about 30% of the water while the drop temperature rises to 0 °C. $^{44-48}$ This creates a mushy water–ice mixture where the remaining liquid water is trapped in a dendritic ice lattice. $^{49}$ Next, the main steady-state freezing front propagates upward in the mushy droplet until complete freezing. We track the main front during the freezing of 5 μL drops on glass and parylene and find a quasiconstant velocity $v \approx 250 \text{ μm/s}$ irrespective of the substrate wettability. At the onset of freezing, the suspension is very dilute and the main front propagates at equilibrium. We can therefore estimate the critical front velocity to repel the particles $v_c$ from models developed for single particles. The most recent one predicts a critical engulfment velocity $v_c \approx 25 \text{ μm/s}$ (see Supporting Information), a value 10 times lower than our main front velocity. Yet, a bright layer is visible above the front during the freezing in Movie S3 indicating a higher concentration of particles there, thus confirming that the particles are initially repelled. Perhaps the particle slight charge and surfactants, not accounted for in the model, have a significant influence here, especially on the magnitude of the DLVO force between the front and the particle. Nonetheless, as the particles concentrate, additional forces come into play, and the particle eventually gets trapped. $^{50}$

We therefore propose a scenario for the stain formation which combines the two mechanisms discussed above. During recrystallization, the front velocity is too high and captures some particles within the dendritic ice lattice. Then, the main front propagates more slowly upward and repels the particles in a liquid lens. $^{35,36}$ At the latter stages of freezing, the pushed particles accumulate in a compacted layer above the solidification front visible in Movie S3 (Figure 6a, the ice lattice

![Figure 6. Schematic representation of the proposed physical process.](https://example.com/figure6.png)

(a) Macroscale: as the freezing front propagates upward, it expels most of the particles toward the top of the drop. The particles thus aggregate in the center, and the aggregation strength depends on the curvature of the liquid lens (which depends on the drop’s aspect ratio). (b) Microscale: Toward the end of the freezing process, the front is not microscopically smooth. Large lamellas propagate forward, leaving large voids, and particles get engulfed between small dendrites, resulting in compact clumps that get deposited on top of each other during sublimation.

CONCLUSION

By freezing colloidal suspension droplets and drying them while solid, we have produced stains that are very different from those obtained by drying liquid drops. In our approach, particles accumulate at the stain’s center to form a porous spot-like core consisting of compact clumps of loosely aggregated particles surrounded by a very thin layer of particle. We have shown that the shape of these stains depends on the initial
geometry of the drop but not on the sublimation rate or substrate roughness. This variation being very nonlinear allows easy control of the stain aspect ratio over several orders of magnitude. This particular structure is the result of the particles being repelled by the solidification front toward the drop apex and their additional concentration during sublimation. Stains from freeze-dried drops therefore offer new opportunities for colloidal deposition, self-assembly, or biomedical assays as they produce a unique porous spot-like structure which is sensitive to a different set of parameters (e.g., front velocity, particle size, or thermal conductivity) that needs further exploration. A better understanding and control of the front–particle interaction during freezing and interfacial capture mechanism during drying could allow the production of ball-like stains with highly ordered porosity similar to the ones recently developed using droplets in solution.49–52

ASSOCIATED CONTENT

2 Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.9b00084.

Time lapse of the sublimation of a drop on a hydrophobic substrate (AVI)
Time lapse of the sublimation of a drop on a hydrophilic substrate (AVI)
Movie of a drop freezing highlighting the clustering of particles toward the drop apex (AVI)
Discussion on the effect of the substrate temperature and drop volume on the stains, and calculation of the critical engulffment velocity based on the model of ref 25 (PDF)

AUTHOR INFORMATION

*Corresponding Author
E-mail: eambon@princeton.edu.

ORCID

Etienne Jambon-Puilet: 0000-0003-2453-0578

Present Address
†Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey 08540, United States.

Notes

The author declares no competing financial interest.

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