

Persistence of Coffee-Ring Deposits in Concentrated Suspensions of Anisotropic Colloids

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Abstract

When droplets of colloidal suspensions evaporate, the suspended colloids are transported to the edge of the drop by an outward radial flow. The resulting dried deposit has a high concentration of colloids along its perimeter, and a low concentration near the center. This effect has been dubbed the coffee-ring effect [Deegan *et. al*, *Nature*, 1997, **389**, 827], and is undesirable in applications such as inkjet printing, where a smooth deposition would lead to more efficient coatings. Previous attempts at suppressing this effect using particle anisotropy have paradoxically shown that anisotropic particles can (1) form even deposits [Yunker *et. al*, *Nature*, 2011, **476**, 308] and (2) enhance the coffee ring effect [Dugyala *et. al*, *J. Phys. Chem. B*, 2014, **119**, 3860]. Here we use surface profilometry data to characterize the width of the dried deposits containing rod-shaped silica colloids of aspect ratios ranging from 1 to 20. We observe deposits over a broad range of concentrations (up to 0.35 volume fraction), and find that the width of the ring is independent of the particle anisotropy, even at previously unexplored high volume fractions. We also observe that polystyrene spheres form more even deposits than silica spheres when evaporated at high temperatures. This result serves to unify the literature by identifying a key parameter in controlling the deposit shape: the difference between the sedimentation velocity of colloids in solution and the velocity of the air-water interface.

1 Introduction

When a colloidal suspension droplet evaporates, a pinned contact-line induces a radial outward flow to replenish the water lost to evaporation along the droplet's perimeter. The result of this is the transport of suspended colloids to the edge of the droplet where they pack together along the air-water interface, leaving a high concentration of colloids along the circumference, and a low concentration of colloids near the center. This effect, first studied in detail by Deegan [1], is known as the coffee-ring effect. Many applications of colloidal suspensions, such as coatings [2], spray-dried liquid-food [3] [2], and ink-jet printing [4] would be made more efficient by smoother and more consistent deposits left upon evaporation. As such, much of the research concerning the coffee-ring effect is focused on its suppression. An emerging picture is that suppression of the coffee-ring effect can be attributed to capture of colloids by the descending air-liquid interface [5–7]. Previous work has shown that parameters which impact the final deposit include temperature [8], surface treatments of both the particle [7] and substrate [9, 10], particle density [11], and particle anisotropy [6, 12, 13]. Particle anisotropy in particular, however, has yielded conflicting results in its ability to suppress coffee-rings. Yunker *et al.* [6] found that suspensions containing elongated polystyrene particles appeared to form smoother deposits than spherical particles, as anisotropic particles can better adsorb to the interface, avoiding transport all the way to the drop edge. Dugyala *et al.* found that suspensions of anisotropic silica and hematite could not be made to form even deposits without adjustments to the suspending medium [12] [14]. Differences in surface chemistry and suspending medium make direct comparison

between existing works difficult, as these factors have been shown to effect deposit formation in other studies [15] [11].

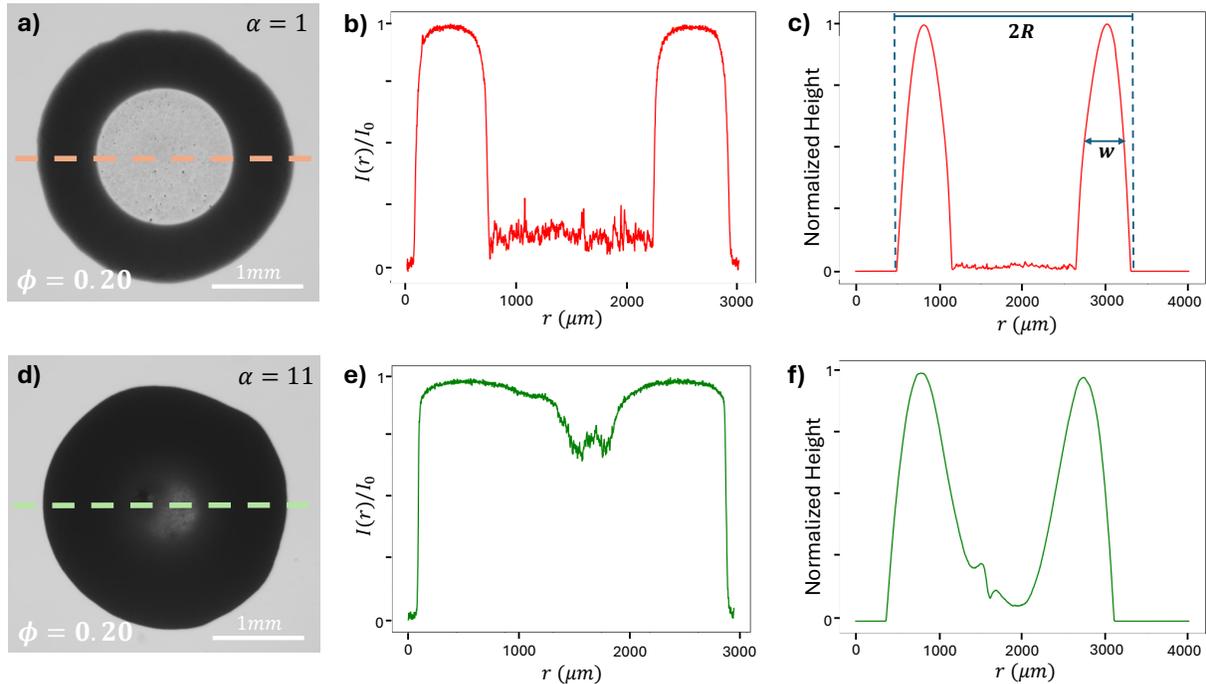


Figure 1: Surface profilometry captures ring deposit geometry. Bright-field microscopy images of deposits formed by (a) aspect ratio, α , 1 and (d) $\alpha = 11$ droplets containing silica particles at $\phi = 0.20$. The scale bars are 1 mm. (b) and (e) show the normalized intensity profiles $I(r)/I_0$ taken along the dashed lines, while (c) and (d) show the result of surface profilometry along the dashed lines. For aspect ratio (α) 1 particles, the coffee-ring is clearly visible in both the intensity profile and surface profilometry. However, for aspect ratio (α) 11 particles, the intensity profile appears even due to saturated absorbance, while profilometry reveals the true coffee ring shape. The coffee ring is characterized by a ring width, w , and a pattern radius, R ; these are labeled in (c).

In this work we thoroughly examine the effect particle anisotropy has on ring formation by evaporating suspensions of silica colloids in water. All anisotropic particles are synthesized using the same method, ensuring that the surface chemistry is unchanged for all aspect ratios. Previous experimental [16] and theoretical [17] investigations into the coffee-ring effect have focused on volume fractions of colloids $\phi < 0.1$ [10, 18]. We measure the ring width over a broad range of volume fractions, up to $\phi = 0.35$, and demonstrate that the effects of anisotropy are not concentration dependent. Surface profilometry is used to make accurate measurements of the deposit's shape and characteristics, even at high concentrations where microscopy techniques can fail to capture ring structure. We also obtain profiles for both silica and polystyrene suspensions evaporated in a 90°C oven and at room temperature, and show that the difference between the sedimentation velocity and the air-water interface velocity is likely responsible for the suppression of the coffee-ring.

2 Materials and Methods

2.1 Synthesis of Silica Particles and Sample Preparation

Charge-stabilized silica spheres (diameter = $300 \pm 30\text{nm}$, $830 \pm 20\text{nm}$) were fabricated using the Stöber synthesis technique, [19,20] and rod-shaped silica particles were created using a one-sided emulsion-nucleation reaction. [21] By varying the temperature of the reaction, different aspect ratio rods were produced. For the rods used in this study, reaction temperatures of 18°C , 27°C , 31°C , and 31°C yielded particles of aspect ratio $\alpha = 3 \pm 0.5$, 7 ± 1.4 , 11 ± 1.4 , and 20 ± 2.3 respectively. All particles were centrifuged and resuspended in ethanol 4 times in order to clean the particles and their medium. Following this cleaning particles were resuspended in MilliQ water for use in experiments. To reduce polydispersity, particle suspensions were centrifuged at 700g for 15 minutes and their supernatants were removed. Leaving the suspensions at 1g for 10 minutes allowed for larger than desired particles to be extracted from the bottom of the solution. Cleaned particles were imaged using a Hitachi S4800 Scanning Electron Microscope (see Figure 2). The diameters and aspect ratios of the particles were characterized from these images using the open source software ImageJ. All error bars reported on particle size and aspect ratio come from the standard deviation from a minimum sample of 20 particles.

The concentration of suspensions were determined by measuring the mass fraction of particles and converting those to volume fraction. The wet and dry mass of $80 \mu\text{L}$ of suspension was recorded on a balance, and the ratio of the dry mass to the wet mass is the mass fraction of the suspension. Since the densities of silica rods and spheres are known, 1.9 g/cm^3 [21] and 2.2 g/cm^3 [22] [23] respectively, the volume fraction of the suspension was thus calculated. Suspensions were then concentrated or diluted to the desired volume fraction in order to perform experiments. The concentrations of suspensions were checked at the beginning and end of experiments and the difference in these values was never larger than 1%.

To test the role of played by particle sedimentation, carboxylated polystyrene spheres (diameter = 288 nm) were procured from Bangs Laboratories Inc. (Fishers, IN) and cleaned 8 times via centrifugation and re-suspension in MilliQ water to remove surfactants from the suspending medium.

2.2 Substrate Preparation and Experimental Procedure

Substrates were prepared as follows. Microscope slides were soaked with a 2.5M solution of NaOH in a 60:40 water to ethanol mixture (by volume) for 2 hours to remove organic contaminants. The slides were then thoroughly rinsed with deionized water for 10 minutes, dried using compressed air, and used immediately for experiments. In order to form droplets for these experiments, $1 \mu\text{L}$ of a colloidal suspension of a known volume fraction was pipetted onto the cleaned glass slide. The outlined procedure resulted in droplet radii between 1.2 mm and 2mm, depending on the concentration of colloids in the droplet. Assuming the drop shape to be a spherical cap, we calculated the drops to have a contact angle between 7° and 35° . The drying process was imaged from below using a microscope setup built in the lab. Most experiments were performed in ambient conditions ($T \approx 20 \pm 2^\circ\text{C}$, $10\% \leq \text{Relative Humidity} \leq 50\%$). Select experiments were performed in high relative humidity conditions ($\text{Relative Humidity} \geq 75\%$). Additional experiments were performed on preheated substrates in an oven set to 90°C .

In order to directly compare to results from the literature [8], commercially acquired polystyrene particles and synthesized silica spheres (diameter = $300 \text{ nm} \pm 30 \text{ nm}$) were dried on a 5mm x 7mm silicon wafer acquired from Ted Pella (Redding, CA). The wafers were rinsed briefly in deionized water, then acetone, and then isopropyl alcohol and dried using compressed air. This procedure resulted in average droplet radii of $1.4 \text{ mm} \pm 0.25 \text{ mm}$, from which we calculated a contact angle of $25.6^\circ \pm 12.8^\circ$.

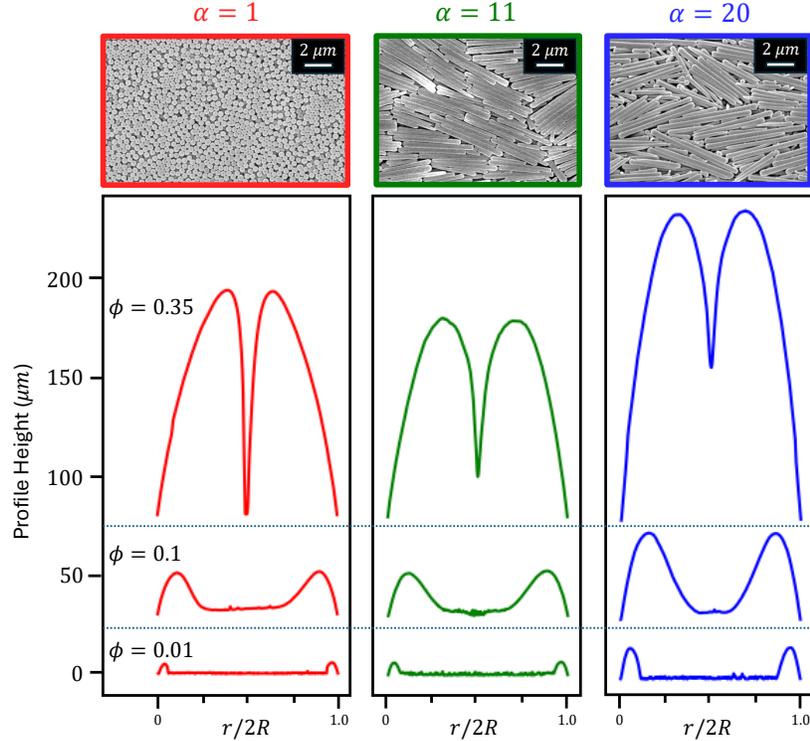


Figure 2: **The volume fraction of the droplet dictates the geometry of ring deposit independent of particle aspect ratio (α).** Profilometry scans for three α : 1, 11, and 20, are shown at three volume fractions: $\phi = 0.01, 0.1, 0.35$. Profiles are vertically offset for clarity, and normalized horizontally by their size $2R$. Increasing volume fraction causes the ring width to increase, while the aspect ratio α has no appreciable effect on the nature of the profile. Above the profile scans are representative SEM images for each aspect ratio, each with a $2\ \mu\text{m}$ scale bar.

2.3 Profilometry Measurements and Analysis

The geometry of the dried deposits were characterized using a Dektak 150 Surface Profilometer. Surface profilometry was chosen to ensure that rings would be accurately observed, even at high volume fractions where microscopy might mischaracterize the deposit due to image saturation. The value of profilometry characterization is clearly illustrated in Figure 1, where top-down imaging and intensity profiles depict a mostly even deposit, while profilometry reveals a distinct coffee-ring. To ensure the deposits were not being damaged by the instrument, scans were repeated several times over the same path and the profiles were found to be identical. Representative profile scans are shown in Figures 1 and 2.

Profilometry data was analyzed with Python routines developed in the lab. Scipy's peak finding function was used to find the peaks' positions and heights. The FWHM were then obtained by finding the first point below the half-maximum on each side of the peaks. The radius of each droplet was found by locating local maxima in the profile's second derivative, corresponding to the edges of the droplet.

3 Results and Discussion

Figure 3 shows the ring widths, w , normalized by droplet radius, R , plotted against the volume fraction for all tested aspect ratios and conditions. We see that the data collapses nicely to a power-law scaling. A

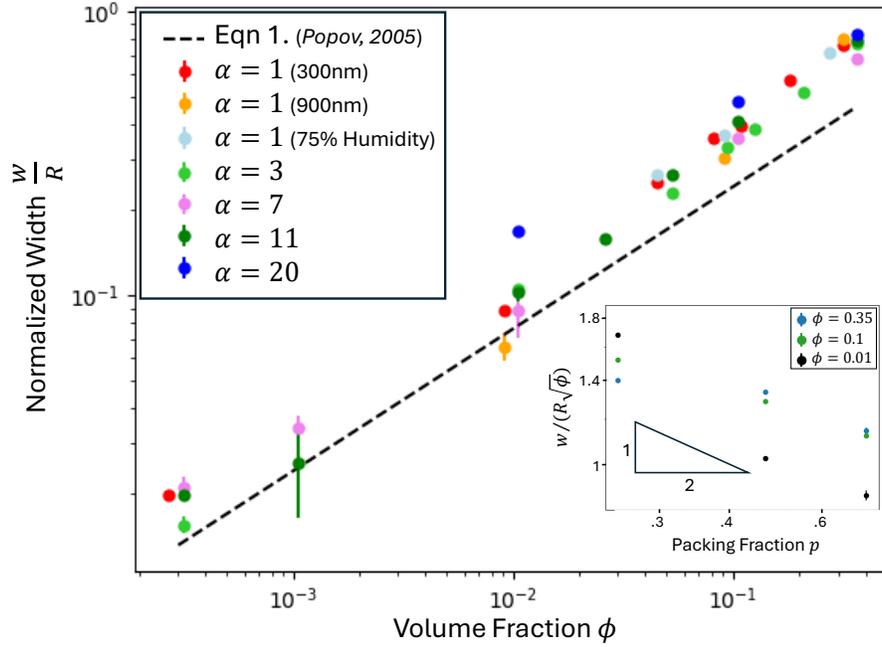


Figure 3: **Coffee-ring geometry does not depend on particle anisotropy.** Normalized widths of the ring shaped deposits formed by droplets containing silica colloids (particle aspect ratio (α) 1-20) are plotted against initial volume fraction. The dashed line (equation 1) is the prediction from Popov [17] using the packing fraction of spheres, $p = 0.64$. The inset shows the dependence of the width as a function of packing fraction for three concentrations, with a triangle representing the power law scaling predicted by 1. The packing fractions are calculated from α using a random contact equation [24].

prediction for this dependence of the width on particle concentration was made by Popov [17]:

$$\frac{w}{R} = 0.609 \sqrt{\frac{\phi}{p}}, \quad (1)$$

where ϕ is the initial volume fraction of colloids and p is the random packing fraction for the colloids' geometry. This prediction (equation 1) was made assuming a low concentration, $\phi < 0.1$, and did not take into account the particle composition nor the cross-sectional geometry of the ring. Surprisingly, Figure 3 shows that our data matches very well with the predicted scaling relationship, even for concentrations greater than $\phi = 0.1$. Given the assumptions under which equation 1 was derived, we do not expect the prefactor to be an exact prediction, as the width predicted by Popov is not necessarily the full-width-half-max as we have measured. This discrepancy is seen in Figure 3 as the dashed line (equation 1) slightly underestimates the ring width.

Equation 1 also tells us that the width should be inversely proportional to the square-root of the packing fraction, p . This relationship is observed in the Figure 3 inset. The packing fraction of ellipsoids is known to decrease with aspect ratio, and it stays near that of spheres until around aspect ratio 10 [24]. This is consistent with our observations, which show that the aspect ratio 11 and 20 data points tend to sit above the rest of the dataset, as we would expect given their significantly lower packing fractions. We also note that our results show strong agreement with the square-root scaling in the high concentration limit, which was not considered in Popov's work [17].

Given that the coffee-ring effect persists over all tested concentrations and aspect ratios, particle shape

alone does not change the characteristics of the deposit, let alone suppress the coffee-ring. Previous work has proposed that the coffee-ring effect is avoided when colloids are captured by the air-water interface during evaporation [6] [8], or when particles quickly sediment and stick onto the substrate [11]. Thus for this study, as well as others which observed rings using ellipsoidal particles [12], have used silica or hematite colloids, both of which have a much higher density relative to water than polystyrene, which has been seen to produce smooth deposits [6] [8]. The key difference here is the sedimentation rate, which is determined by the colloid’s density and size. From Stoke’s law we can write the terminal velocity of a sedimenting colloid,

$$v_p = \frac{2\Delta\rho gR^2}{9\eta} \quad (2)$$

where $\Delta\rho$ is the difference in density between the colloid and the suspending medium, g is the acceleration due to gravity, R is the radius of the particle, and η is the dynamic viscosity of the liquid. For polystyrene, the difference in density of the particles from that of water is 0.05 g/cm^3 while for silica spheres it is 1.2 g/cm^3 . At room temperature (22°C), the sedimentation velocity of the silica colloids is $0.234 \text{ }\mu\text{m/s}$ and for polystyrene is $0.009 \text{ }\mu\text{m/s}$. Thus, for a range of interface velocities, the descending air-water interface can capture the polystyrene, but move too slowly to capture the silica. Once the particles are captured on the surface, they assemble into a structure which grows towards the center of the droplet, accumulating other surface-captured particles before they can reach the edge [7]. This can then result in a more even dried deposit.

The velocity of the descending interface, v_i is controlled by the evaporation rate. Thus, to examine how changes in v_i alter deposit patterns, we obtained profiles for silica and polystyrene sphere suspensions dried at room temperature and in at 90°C . Figure 4 shows these profiles, and we can observe that the deposition of polystyrene particles can be smoothed by increasing the system’s temperature, in agreement with measurements reported by Li et al. [8]. Silica particles, on the other hand, continue to form rings, even at high temperatures. The effect of temperature on geometry can be understood by examining the dependence of v_p and v_i on temperature. As the temperature increases both velocities increase, but by vastly different amounts: v_p increases threefold due the reduction in η , while the interface velocity increases by over an order of magnitude [8]. This means that the interface is faster relative to the colloids at higher temperatures than it is at lower temperatures, enhancing adsorption to the interface. Figures 3 and 4 demonstrate that particle shape alone cannot control the deposition pattern, nor can temperature. It is a combination of these factors and others that allow for the colloids to be caught by the air-water interface, forming a smooth deposition. While others have tested the effects of these variables before [8, 11, 12], here we have shown the importance of considering all sources of coffee-ring suppression when comparing results, as this suppression is controlled by many system parameters. [7, 8, 14]

4 Conclusions

Tuning the deposit pattern formed by evaporating colloidal suspensions is desirable for many applications, such as inkjet printing. Here, we have shown that particle anisotropy is not a sole determining factor in the dried deposition pattern. In fact, in a solution of silica colloids, changing particle anisotropy has no appreciable effect on the characteristics of the deposit. Rather, the profile of the deposit is determined by the surface capture effect, which in turn is controlled by many parameters including particle shape, particle density, temperature [8], surfactant concentration [14, 25], and the particle surface treatment [7]. In exploring the effect of anisotropy we observed deposit profiles consistent with those seen [8] and predicted [26] previously. We also demonstrate that characterizing the coffee-ring effect is best done using profilometry techniques rather than light microscopy, and that the width of the coffee-ring is a useful and well-predicted metric for quantifying the effect control parameters have on the dried deposit. Coffee-ring formation is

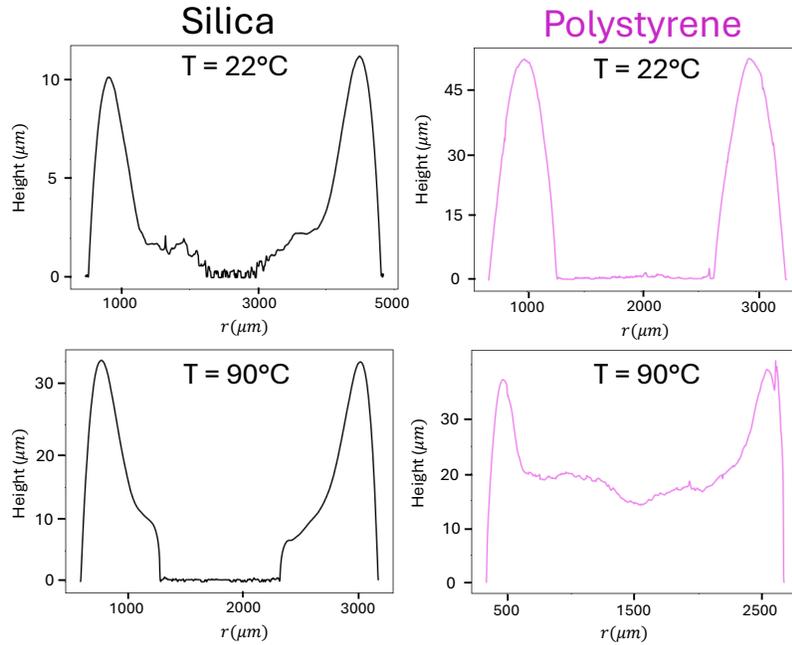


Figure 4: **Deposits become smoother when particles are more easily captured by the interface** Deposits formed from $\phi = 0.05$ silica (left) and polystyrene (right) at 22°C (top) and 90°C (bottom). Profiles exhibit a clear ring shape, except for polystyrene evaporated at 90°C (bottom right). At higher temperatures, the air-water interface moves fast enough to capture polystyrene during evaporation, resulting in a more uniform deposit. However, denser silica particles sediment too quickly to be captured by the interface before being carried to the droplet edge.

intrinsically linked to particle surface capture, and thus is sensitive to particle surface chemistry, substrate preparation, and the components of the suspending medium. This sensitivity makes it crucial to consider all possible sources of ring-suppression when it is observed.

Author Contributions

S.S.N. contributed to the experimental design, data acquisition and analysis, interpretation, and drafted and edited the manuscript. B.C.S. contributed to the conception of the work, experimental design, interpretation, data acquisition and analysis. M.M.D. contributed to the conception of the work, interpretation, and edited the manuscript.

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