Coalescence, evaporation and particle deposition of consecutively printed colloidal drops

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The particle deposition dynamics of two consecutively printed evaporating colloidal drops is examined using a fluorescence microscope and a synchronized side-view camera. The results show that the relaxation time of the water–air interface of the merged drop is shorter than that of a single drop impacting on a dry surface. It is also found that both morphology and particle distribution uniformity of the deposit change significantly with varying jetting delay and spatial spacing between two drops. As the drop spacing increases while keeping jetting delay constant, the circularity of the coalesced drop reduces. For the regime where the time scale for drop evaporation is comparable with the relaxation time scale for two drops to completely coalesce, the capillary flow induced by the local curvature variation of the air–water interface redistributes particles inside a merged drop, causing suppression of the coffee-ring effect for the case of a high jetting frequency while resulting in a region of particle accumulation in the middle of the merged drop at a low jetting frequency. By tuning the interplay of wetting, evaporation, capillary relaxation, and particle assembly, the deposition morphology of consecutively printed colloidal drops can hence be controlled.

1. Introduction

Deposition morphology of colloidal drops consisting of solution-processed functional materials is crucial in applications such as inkjet and gravure printing, spray deposition of printable electronics, photovoltaics, and micro-batteries.1–4 With the development of vastly available organic and inorganic ink materials consisting of nano-metallic particles, semiconductor quantum dots and nanowires, conducting polymers, among others, of different shapes and functionalities,5–7 the challenge now is to effectively assemble these nano-scale building blocks into useful meso-scale structures.8 Particle assembly by capillary interactions driven by the decrease in liquid–vapor (L–V) surface area as the particles approach each other has become an area of active research.9,10 Deposition of evaporating colloidal drops consisting of monodispersed spherical particles leads to the well-known coffee-ring effect as a result of the evaporatively driven flow that carries particles to deposit in the vicinity of the drop contact line.11,12 The suppression of the coffee ring by shape-dependent capillary interactions has also been observed for deposition of colloidal drops consisting of ellipsoidal particles.13 Understanding particle deposition from a single colloidal drop is important. However, drops are often used as building blocks for line and pattern printing where the interaction between drops plays an important role in determining the morphology of deposited functional materials.

A number of studies have been carried out to examine the dynamics of sessile drop coalescence by making two drops of pure liquid slowly come into contact with each other.14–18 The process of drop coalescence can be distinguished into three physical stages: (i) the initial stage where the edges of two droplets make contact and quickly form a thin liquid bridge which increases in width following a temporal power law, (ii) the intermediate stage where the meniscus bridge relaxes, the contact line of the droplets begins to move (i.e., wetting on one side while dewetting on the other side), and the curvature of the drop surface above the initial contact point changes from concave to convex, and (iii) the final stage where the combined drop relaxed toward a spherical cap, the minimum surface energy configuration. The dynamics of time-dependent width of the meniscus bridge between the two merging droplets,14,15,19 and the perimeter18 and shape20 of the merged drop have been studied as a function of the liquid viscosity, surface tension, and density as well as the substrate wettability. It was found that the merged drop slowly relaxes to a spherical cap where the characteristic relaxation time is proportional to the drop radius of the final equilibrium. This relaxation time is several orders of magnitude larger than the bulk capillary relaxation time due to the strong dissipation of the moving contact line.18

Drops impacting upon a dry or a wet surface can result in different morphologies, from spreading and splashing to receding and rebounding, depending on the impact velocity, drop size, properties of the liquid and substrate.21 Spreading or
“deposition” is observed for the case of a low-velocity impact. The impact and coalescence of a pure liquid drop onto a pre-deposited drop of the same liquid have been studied with a varying offset between the centers of two drops.\(^{22-24}\) It was found that, for the case of no offset and in the low Weber number regime (\(\text{We} = \rho D_0 U_0^2/\sigma\)), where \(\rho\) is the density, \(D_0\) the diameter, \(U_0\) the velocity of the droplet before impact, and \(\sigma\) the surface tension), axisymmetric impact and spreading lead to a merged drop of a spherical cap shape following the kinematic, spreading, and relaxation phases.\(^{25}\) As the distance between two drop centers increases, the impacting drop lands on a pre-wetted region of the substrate and the resulting merged drop exhibits a circular footprint, similar to the no offset case. When the distance between drops is larger than the extent to which the first drop spreads, the impacting drop lands on a dry surface and two drops coalesce after the initial impact and wetting stages of the second drop. When the droplet separation is close to the maximum distance that still results in a contact between drops, the impacting droplet fully spreads and then two droplets coalesce in a similar fashion as two static drops.

The discussion until now has been based on pure liquid drops where evaporation is negligible. Recently, the deposition morphology of inkjet-printed solution or suspension into line patterns has been explored. For example, Duineveld\(^{26}\) studied the stability of inkjet-printed lines consisting of PEDOT:PSS, a conducting polymer, using a single-nozzle drop-on-demand inkjet printer. It was shown that the printed line becomes unstable and causes the bulging effect when its contact angle is larger than the static advancing contact angle. Stringer and Derby\(^{27}\) concluded that the stable line width of a printed line is bound by the minimum line width determined by the maximum drop spacing for stable coalescence and the upper bound determined by the minimum drop spacing below which a bulging instability occurs. Based on these analyses, appropriate printing parameters and ink/substrate properties can be selected to warrant optimal deposition uniformity and line definition. However, the studies of Duineveld\(^{26}\) and Stringer and Derby\(^{27}\) are mostly concerned with the instability of the contact line. To the best of our knowledge, no information on the deposition dynamics of particles inside interacting colloidal drops is known.

In this paper, the interaction between two consecutively printed evaporating colloidal drops and the resulting particle deposition morphology are systematically studied as a function of the temporal delay and spatial spacing between drops. Pico-liter colloidal drops produced by an inkjet printer represent a common drop size widely used for high-resolution materials printing applications. On such length scales, capillary and evaporation are the dominating mechanisms, whereas the gravitational effect is negligible. Three different regimes of drop spacing, \(d\), are considered. The second drop is either printed (i) on the pre-wetted region of the substrate by the first drop (short drop spacing, \(0 < d < 0.5 \, D_c\), where \(D_c\) is the maximum spreading diameter of the first drop on the substrate), (ii) on a dry surface very close to the pinned contact line of the first drop (medium drop spacing, \(0.5 \, D_c < d < 0.75 \, D_c\)), or (iii) on a dry surface away from the first drop so that the second drop is allowed to spread after the initial impact and then coalesces with the first drop (long drop spacing, \(0.75 \, D_c < d < D_c\)). For the case of \(d > D_c\), the interaction between drops is prohibited and the deposition of the second drop will be the same as the first drop. We focus on the regime where the drop jetting delay is comparable with or an order of magnitude smaller than the drop evaporation time scale. In addition, the relaxation time for two consecutively printed drops to completely coalesce in a saturated environment is on the same order of magnitude as or slightly longer than the drop evaporation time. Due to the presence of colloidal particles and carrier liquid evaporation, drop coalescence is constrained. In such conditions, multiple mechanisms simultaneously determine the drop interaction and particle deposition. This makes a single model that correlates ink/substrate properties and jetting parameters with the final deposition morphology either impossible or very difficult. In the present study, by using a fluorescence microscope and a synchronized side-view camera, we directly observe in real time the interplay between the evaporation of the first drop, impact and spreading of the second drop, capillary relaxation, microflows, evaporation, and particle deposition of the merged drop for better control of the deposition morphology of inkjet-printed functional materials.

2. Experimental details

The inkjet printing setup integrated with a synchronized flash photography system for side-view imaging and a fluorescence microscope for the bottom-view observation is depicted in Fig. 1. A waveform generator (JetDrive) is used to adjust the voltage waveform driving the piezoelectric nozzle. In the humidity chamber, the piezoelectric inkjet print head with a diameter of 60 \(\mu\)m (MicroFab MJ-Al-01) is used to generate pico-liter drops. A high resolution (0.5 \(\mu\)m per pixel) SensiCam QE CCD camera (Romulus, Michigan) with a Navitar 12\(\times\) Zoom lens (Rochester, New York) and a halogen strobe light (Perkin Elmer) are used to capture side-view images of drop coalescence. The flash photography technique introduced by Dong et al.\(^{28}\) is used to

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**Fig. 1** Schematic of the inkjet printing experimental setup.
obtain side-view images where the ability to form repeatable drops is assumed. During evaporation of colloidal drops, the particle motion and deposition are observed by using a Zeiss inverted fluorescence microscope (Thornwood, New York) with a 40× oil objective. Bottom-view images are captured by a Sony XCL-5005CR CCD camera (Park Ridge, New Jersey) at 10 frames per second. The waveform generator, two CCD cameras and the strobe light are synchronized with a delay generator (SRS DG645, Sunnyvale, California). Other detailed information of the experimental setup was previously introduced in Chhasatia and Sun.29

To observe the particle movement and the evaporation of colloidal drops, a colloidal mixture of carboxylate-modified polystyrene fluorescent beads (Invitrogen) of 1.1 μm diameter in DI-water, 0.2% by volume, is used in our inkjet printing experiments. The mixture of water and particles is homogenized in a sonicator (Cole-Parmer 8891) for 15 minutes before printing. The diameter of the drop is 68 μm and the velocity for the colloidal drop upon impact on cleaned glass substrates (Belco, ~150 μm thick) is around 1.9 m s⁻¹. The corresponding Weber number and Ohnesorge number (Oh = μ/√ρD₀, where μ is the liquid viscosity) are 2.1 and 0.014 respectively. The substrates are cleaned with a sequence of DI water, acetone, ethanol, and isopropanol three times and then dried with compressed air. During the experiments, the ambient temperature and humidity are kept at 20 °C and 50% relative humidity. Image processing is performed in IMAGEnJ (http://rsbweb.nih.gov/ij/).

Two colloidal drops with controlled jetting delay and spatial spacing are printed consecutively to observe interactions between them. The drop spacing is controlled by a high-resolution motorized microscope stage (Ludl) and the jetting delay between two drops is created by the JetDrive. For printing of colloidal drops, the jetting delays between two drops are 0.2 s, 0.6 s and 0.9 s, and the drop spacing varies from 38 μm to 105 μm. The Bond number (Bo = ρgD₀²/σ, where g is the gravitational acceleration) of our printed drops is less than 0.005 where the gravitational distortion of the drop shape is neglected.

3. Results and discussion

A. Drop coalescence

Side-view images for the coalescence of two consecutively printed evaporating colloidal drops on a cleaned glass substrate (Belco, ~150 μm thick) are shown in Fig. 2a, where the jetting delay between two drops is 0.6 s and the drop spacing is 73.4 μm (i.e., 0.7 D₀, where D₀ is the maximum spreading diameter of the first drop on the substrate). Initial observation shows that it takes 1.3 s for a single drop to evaporate. The contact line of the first drop is pinned right after the drop impact and spreading. It is noted here that the static receding contact angle measured using a DI-water drop on a cleaned glass substrate is 23°. However, the accumulation of particles along the drop edge prolongs the pinning of the contact line for the case of a colloidal drop. When a second drop impacts on the right side of the substrate (at t = 0 in Fig. 2a) 0.6 s after the first drop is deposited, the inertia from its impact on the dry surface drives the second drop to come into contact with the first drop within 10 μs. The merged drop continues to spread due to the interplay of inertia, viscous stress, and surface tension. The drop contact line becomes pinned at t = 30 μs and it is followed by both vertical and horizontal oscillations of the water–air interface. After the oscillations are damped by viscosity, the water–air interface exhibits an arc shape at t = 300 μs, where both left and right contact angles of the merged drop converge to a contact angle of 45°. During this first 300 μs, the effect of evaporation, which has the time scale on the order of seconds, can be neglected.

It is important to note that the relaxation time of the water–air interface of the merged drop is much shorter than that of a single drop impacting on a dry surface. As shown in Fig. 2b, in the first 300 μs upon impact, the drop spreads on the dry surface and oscillates vertically and symmetrically where the contact angle fluctuates between 70° and 90°. After 300 μs, the drop continues to spread and it takes over 1 ms for the single drop to relax to its equilibrium contact angle. It is shown in a comparison study of drop impacting on dry and wetted surfaces that both the impact morphology and spreading dynamics vary significantly with the type of surface.30 Riiboo et al.31 also found that the drop spreading dynamics is less sensitive to the surface tension, impact velocity, and viscosity for a wetted surface as compared to a dry surface. In the present study, however, the impact of the second drop is either on the edge of an evaporating drop or on a dry surface close to an evaporating drop, where the drop impact and spreading are expected to show combined characteristics of both dry and wetted surfaces.

Andrieu et al.18 suggested that the rate of relaxation of a slightly deformed drop to a spherical cap can be distinguished into three characteristic time scales: the inviscid inertial time (tᵢ ~ μs), viscous inertial time (tᵢ ~ ms) and capillary relaxation time (tᵢ ~ μs). The inviscid inertial time, tᵢ, during which the liquid is compressed and a shock wave is formed can be given by

$$tᵢ = \frac{\sqrt{\rho R^3}}{\sigma}$$ (1)

where R is the radius of the drop in flight. The viscosity then damps the oscillation on a time scale of

$$tᵢ = \frac{R^2}{ν}$$ (2)

where ν is the kinematic viscosity. Finally, the viscous relaxation driven by the surface tension is

$$tᵢ = \frac{ν R}{σ}$$ (3)

All three time scales are much smaller than the evaporative time scale (on the order of a second) and are comparable to or smaller than the steady-state diffusion time (~ms), tᵢ = 4R²/D. For a drop of 68 μm in diameter, the total relaxation time (tᵢ + tᵢ + tᵢ) is about 1.2 ms. When the second drop impacts on the substrate 0.2, 0.6, or 0.9 s after the first drop is deposited, the first drop has already equilibrated and can act as a buffer to effectively damp the oscillation resulted from the impact of the second drop (e.g., the relaxation time of the merged drop reduces to 300 μs from over 1 ms for a single drop impacting on a dry surface as discussed earlier).

Andrieu et al.18 also shows, for coalescence of two water drops of a similar size as the ones considered here (~50 μm in diameter), the relaxation time of the merged drop in a nitrogen
environment saturated with water vapor is on the order of $5\, s$, $10^7$ larger than the bulk capillary relaxation time, $t_b$. In such a case, the dynamics of drop coalescence is controlled by the receding motion of the contact line. The dissipation due to the gas–liquid phase transition near the contact line introduces a very small $K \sim 10^{-8}$ Arrhenius factor in relation between the driving force and the contact line velocity. In the present experiment, two drops coalesce at $20\, ^\circ C$ and $50\%$ relative humidity, where the merged drop evaporates in less than $3\, s$. The subsequent particle accumulation at the contact line due to the evaporatively driven flow enhances contact line pinning and hence leads to incomplete drop coalescence before the carrier liquid completely evaporates.

Although the water–air interface appears to reach equilibrium at $t = 300\, \mu s$ from the side-view image shown in Fig. 2a, the merged drop is still not completely coalesced, indicated by the shape of its footprint observed from the bottom-view image (see Fig. 5b). Fig. 3 shows schematic illustrations from both the side and bottom views of the drop impact, coalescence, carrier liquid evaporation, and particle deposition processes of two consecutively printed evaporating colloidal drops. As it can be seen, before the impact of the second drop, the contact line of the first drop is pinned and the evaporatively driven flow drives particles to deposit near the contact line region and further enhances pinning. As the second drop lands on one side of the first drop, the inertia drives the liquid to merge into the first drop. As the merged drop spreads and the water–air interface vibrates, it creates variations in the local contact angle, relaxation velocity, and local mean radius of curvature of the air–water interface. These local variations drive liquid to flow back and forth between two drops and bring particles along with it. Once the water–air interface reaches equilibrium, the mean curvature difference between the first and second drops drives the liquid to flow into the first drop side due to the local pressure difference $\Delta p = p_{d1} - p_{d2}$, where $p_{d1}$ is the pressure on the first drop side and $p_{d2}$ is the pressure on the second drop side and both are determined by averaging the local capillary pressure.

Fig. 2  Side-view images for the impact and coalescence of two consecutively printed drops compared to the impact of a single drop on a dry surface during the same time frame. The jetting delay between two drops is $0.6\, s$ and the drop spacing is $73.4\, \mu m$ (i.e., $0.7\, D_c$, where $D_c$ is the maximum spreading diameter of the first drop on the substrate). Other conditions for the two consecutively printed drops and the single drop are identical. For the case of a single drop, the drop continues to spread after $300\, \mu s$ until it reaches an equilibrium contact angle of $45^\circ$.
Fig. 3  Schematic of drop impact, coalescence, carrier liquid evaporation, and particle deposition of two consecutively printed evaporating colloidal drops from the side view (left) and bottom view (right) based on the medium drop spacing (0.5 $D_c < d < 0.75 ~D_c$) and long jetting delay (0.9 s) case.

$$p(x, y) = \sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right)$$  \hspace{1cm} (4)

Here $R_1$ and $R_2$ are the principal radii of curvature at any point $(x, y)$ on the water–air interface. Because the second drop only spreads partially before it merges with the first drop whose contact line is pinned, the mean radius of curvature of the air–water interface on the second drop side is smaller than that of the first drop side. This curvature variation along the contact line leads to a flow inside the merged drop from the right to the left as shown in Fig. 3e. When the merged drop continues to coalesce and evaporate, its footprint relaxes towards a circular shape while the evaporatively driven flow brings particles to the contact line region and deposit there.

B. Drop evaporation and deposition morphology

Fig. 4(a)–(c) show evolution snapshots of two consecutively printed colloidal drops with a 0.9 s delay time and short (0.4 $D_c$), medium (0.7 $D_c$), and long drop spacings (0.95 $D_c$), respectively, where $D_c$ is the maximum spreading diameter of the first drop on the substrate. For the case with 0.4 $D_c$ of spacing between two drops (Fig. 4a), the second drop impacts on top of an evaporating drop at $t = 0.9$ s and two drops merge immediately upon impact. It is shown from the side-view images that the water–air interface of the merged drop relaxes to an arc shape before $t = 1.0$ s (the third snapshot). Because the contact line of the first drop is pinned when the second drop impacts on it, the surface tension pulls the second drop to merge with the first drop and hence limits the spreading of the second drop. The merged drop shows an asymmetric footprint with a smaller mean radius of curvature of the air–water interface on the second drop side and the curvature continuously varies along the perimeter of the merged drop at $t = 1.0$ s. In addition to the evaporatively driven flow as observed in evaporation of single drops, the motion of the particles from the second drop to the first drop is observed due to the pressure imbalance that pushes the liquid to flow from the second drop (smaller radius of curvature) to the first drop side (larger radius of curvature) and drags particles along with it. The contact line of the merged drop is pinned and the particles move to the edge of the drop that results in a coffee-ring deposit, with a larger particle concentration on the first drop side.

As the spacing between two drops increases to 0.7 $D_c$ (Fig. 4b), the second drop impacts on a dry surface and spreads symmetrically before it comes into contact with the first drop. The water–air interface of the merged drop relaxes to an arc shape and the footprint of the merged drop displays two deposition centers with a neck region connecting in the middle. The coffee-ring deposit that already formed along the pinned contact line of the first drop before it coalesces with the second drop remains stable, which leaves a higher particle density region in the middle of the two drop centers.

When the spacing between two drops reaches 0.95 $D_c$, the second drop is allowed to spread more until its wetting front approaches the pinned contact line of the first drop. Once the merged drop coalesces, the imbalance in capillary pressure inside the drop drives the liquid to flow from the second to the first drop, resulting in local depinning of the contact line in the second drop side. The final deposition presents a higher particle density region in the original first drop region compared to the second drop. As the separation distance between two drops increases, the area and length of the deposition increase.

Fig. 5 shows evolution snapshots of two consecutively printed colloidal drops with similar separation distances, but with delay times of 0.2, 0.6, and 0.9 s, respectively. The separation distance in all three cases are in the medium (0.6–0.7 $D_c$) separation regime where the second drop impacts on a dry surface and spreads briefly but symmetrically before it comes into contact with the first drop. For the case of a short jetting delay (Fig. 5a), only a small amount of liquid in the first drop evaporates (the evaporation time for a single drop is 1.3 s) before it coalesces with the second drop. The two drops quickly merge and spread into a single drop of an elliptical footprint and the deposition is symmetric on both the first and second drop sides. No accumulation of particles along the contact line of the first drop is detected in the final deposition. The maximum dimension of the deposit perpendicular to the axis that connects the centers of the two drops (i.e., the major axis) is larger than the diameter of a single drop.
As the jetting delay between two drops increases, the effective total volume of the merged drop decreases due to the increase in evaporation time of the first drop. For the case of 0.6 s delay (Fig. 5b), particle accumulation at the contact line of the first drop occurs before the second drop coalesces with it. The pinned contact line on the first drop side prevents spreading of the merged drop in the direction perpendicular to the major axis. Liquid flows from the second to the first drop due to mean curvature variation of the air–water interface. The final deposition exhibits a smoothly connected pattern with a smaller radius of curvature on the second drop side. When the jetting delay reaches 0.9 s, a coffee-ring pattern is already established in the first drop before the deposition of the second drop. The presence of the coffee ring from the first drop increases the non-uniformity of the deposit as compared with the cases of shorter jetting delay.

To quantify the particle distribution inside the merged drop, the scaled particle number density along the major axis of the deposit from two consecutively printed drops for the medium drop spacing cases (i.e., $0.5 D_c < d < 0.75 D_c$, where the second drop impacts on a dry surface but spreading is limited due to the presence of the first drop) and jetting delays of 0.2, 0.6, and 0.9 s is plotted in Fig. 6. The particle number density is measured in a $36 \mu m \times 18 \mu m$ wide stripe area along the major axis, $x$, and each grid is $18 \mu m$ long. The scaled particle number density is defined as $n^* = A_{\text{drop}} n_p / A_{\text{grid}} n_{\text{total}}$ where $A_{\text{grid}}$ is the area of each $36 \mu m \times 18 \mu m$ grid along the major axis, $A_{\text{drop}}$ is the area enclosed by the drop contact line inside each grid, $n_{\text{total}}$ is the total number of particles inside the $36 \mu m$ stripe area along the major axis, and $n_p$ is the number of particles inside each grid. The first data point of each case starts in the center of the first $36 \mu m \times 18 \mu m$ grid along the major axis not at the exact edge of the deposition ($x = 0$). It can be observed for all three cases that the scaled particle number density peaks at both ends of the major axis, an indicator of the coffee-ring effect. In addition, the peak on the first drop side is higher than the second drop side as a result of the capillary flow due to mean curvature variation of the air–water interface. For the case of a large jetting delay between two drops (i.e., 0.9 s delay), a third peak is observed in the middle of two drops where the pinned contact line of the first drop is located before the impact of the second drop (i.e., $x = D_c$). However, for the cases of small jetting delays (0.2 and 0.6 s delays), the particle number density in the center of the merged drop is fairly uniform. This implies that the deposition uniformity can be improved by increasing the jetting frequency. It is also noted that the scaled number density is based on the average of three jetting experiments for each jetting delay and the standard divisions of all cases of the same jetting conditions are within $\pm 0.03 D_c$. It might be argued that there is also a small increase in $n^*$ for the case of 0.2 s jetting delay at $x \approx 0.6 D_c$. However, compared to a 31% increase in $n^*$ for the 3rd peak of the 0.9 s delay case at $x \approx 0.6 D_c$, this 11% increase in $n^*$ is not substantial enough to be viewed as a peak. It is important to note that the long jetting delay of 0.9 s considered here is comparable to the 1.3 s evaporation time of a single drop.

Scaled radii of curvature of the contact line, $r^* = r R_c$ ($R_c = D_c / 2$), on the second drop side of the merged drop as a function of the scaled drop spacing for 0.2, 0.6, and 0.9 s jetting delays are
shown in Fig. 7. The radii of curvature of the contact line are measured based on the bottom-view images right after two consecutively printed colloidal drops coalesce. It is shown in Fig. 7 that, for the delay time of 0.2 s, the scaled radius of curvature of the contact line on the second drop side decreases monotonically with the scaled drop spacing. This is because, for a

short jetting delay, two drops completely coalesce and a larger drop spacing leads to a more elongated shape for the merged drop. For the cases of longer jetting delays (0.6 and 0.9 s), the radius of curvature of the contact line on the second drop side decreases first as the merged drop becomes more elongated, and then $r^*$ increases with the increase in drop spacing where the transition occurs at around 0.7 $D_c$, the drop distance where the
curvature of the contact line in the neck region between two drops changes from convex to concave. This indicates that two deposition centers are observed with a neck region connecting them for the case of large drop spacing and long jetting delay. In such cases, the second drop is allowed to spread more before it coalesces with the first drop, and hence \( r^* \) increases with the increase in drop spacing. For the same drop spacing, a shorter jetting delay corresponds to a larger \( r^* \). Because a shorter jetting delay leads to a larger drop volume, the merged drop can further relax to a circular footprint before the carrier liquid completely evaporates.

Fig. 8 shows the circularity of the coalesced drop as a function of the scaled drop spacing for jetting delays of 0.2, 0.6, and 0.9 s. The circularity is measured based on the first bottom-view image after two drops coalesce, using circularity = \( 4\pi \times \) footprint area/(contact line perimeter)\(^2 \). As it can be observed, higher circularities are obtained for shorter jetting delays compared with longer delays for all short, medium, and long drop spacing cases. This is because, for the same drop spacing, a short jetting delay allows for more liquid remained in the merged drop so that the neck region connecting two drops can spread more extensively to yield a more circular footprint that minimizes the surface energy. For the same jetting delay (which implies the same drop volume), the circularity of the merged drop decreases with the increase in drop spacing. This is because, especially for smaller jetting delays, the footprint of a merged drop exhibits an elliptical shape. If an equilibrium contact angle is assumed when the merged drop fully relaxes, the height of the elliptical cap formed by the merged drop is the same for different drop spacing cases. This implies that the product of the minor and major axes of ellipse remains constant for different drop spacings. When the drop spacing increases, the increase in the ratio between the major and minor axes results in a decrease in circularity of the merged drop as shown in Fig. 8. For all three jetting delays considered in this study, the circularities are larger than 0.92 for the short drop spacing regime (0 < \( d < 0.5 \, D_c \)). However, with the increase in drop spacing for the cases of long jetting delays (0.6 and 0.9 s delays), as is shown in Fig. 4c, a clear neck region is observed between the first and second drops and hence results in poor deposition circularity.

4. Conclusions

The dynamics of drop interaction and particle deposition of two consecutively printed evaporating colloidal drops are observed in real time using a fluorescence microscope and a synchronized side-view camera. The second drop is printed either on the pre-wetted region of the first drop (short drop spacing, \( 0 < d < 0.5 \, D_c \)), on a dry surface very close to the pinned contact line of the first drop (medium drop spacing, \( 0.5 \, D_c < d < 0.75 \, D_c \)), or on a dry surface away from the first drop so that the second drop is allowed to spread and then coalesces with the first drop (long drop spacing, \( 0.75 < d < D_c \)). The jetting delay considered here is either comparable with or an order of magnitude smaller than the drop evaporation time. The results show that the relaxation time of the water–air interface of the merged drop is shorter than that of a single drop impacting on a dry surface. As the drop spacing increases, the circularity of the coalesced drop decreases for all jetting delays. Moreover, for the drops interacting with a longer jetting delay, a coffee ring has already been established before the impact of the second drop. As the second drop impacts on the substrate and coalesces with the first drop, the capillary force and inertia drive the carrier liquid and suspended particles in the second drop toward the first drop resulting in more particles deposited on the first drop side. The particle number density along the major axis of the deposit shows two peaks at the two ends of the major axis for the cases with shorter jetting delays, but a third peak located at the contact line of the first drop is observed for a longer jetting delay. For a short jetting delay, the scaled radius of curvature of the contact line on the second drop side of the deposit decreases monotonically with the scaled drop spacing, but it decreases first and then increases with the increase in drop spacing for larger delays.

In contrast to other drop coalescence studies, inertia, evaporation, and particle deposition all play important roles in the deposition morphology of the merged drop for the conditions considered here. In addition, the present study reveals the deposition dynamics of individual particles in coalescing colloidal drops in real time when the drop contact line is pinned. By tuning the interplay of drop spreading, evaporation, capillary relaxation, and particle assembly processes, the deposition morphology of two consecutively printed colloidal drops can hence be controlled.

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