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The effect of particle wettability on the stick-slip motion of the contact line

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ABSTRACT. Contact line dynamics is crucial in determining the deposition patterns of evaporating colloidal droplets. Using high-speed interferometry, we directly observe the stick-slip motion of the contact line *in situ* and are able to resolve the instantaneous shape of the inkjet-printed, evaporating pico-liter drops containing nanoparticles of varying wettability. Integrated with *post-mortem* optical profilometry of the deposition patterns, the instantaneous particle volume fraction and hence the particle deposition rate can be determined. The results show that the stick-slip motion of the contact line is a strong function of the particle wettability. While the stick-slip motion is observed for nanoparticles that are less hydrophilic (i.e., particle contact angle $\theta \approx 74°$ at the water-air interface) which results in a multi-ring deposition, a continuous receding of the contact line is observed for more hydrophilic nanoparticles (i.e., $\theta \approx 34°$) which leaves a single-ring pattern. A model is developed to predict the number of particles required to pin the contact line based on the force balance of the hydrodynamic drag, interparticle interactions, and surface tension acting on the particles near the contact line with varying particle wettability. A three-fold increase in the number of particles required to pinning is predicted when the particle wettability increases from the wetting angle of $\theta \approx 74°$ to $\theta \approx 34°$. This finding explains why particles with greater wettability form a single-ring pattern and those with lower wettability forms a multi-ring

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pattern. In addition, the particle deposition rate is found to depend on the particle wettability and vary with time.

1. Introduction

The motion of the contact line during evaporation of thin films,[1–3] menisci,[4–9] and droplets[10–12] is important in natural and industrial processes from the drying of tear films[13,14] to coating and printing technologies.[15–18] The evaporation of a sessile drop often involves three distinct stages:[19–21] the constant contact area mode where the contact line is pinned, followed by the constant contact angle stage where the contact line depins, and finally the mixed mode where both the contact area and contact angle decrease. The addition of particles in evaporating colloidal drops enhances the pinning of the contact line due to the accumulation of particles along the drop edge induced by the evaporation-driven flows. For such cases, the decrease in contact angle due to evaporation is offset by the increase in contact angle caused by the protrusion of particles to the contact line,[20] resulting in delays in the second and third stages of evaporation and the well-known coffee-ring deposition.[10] Additionally, a self-pinning mechanism of colloids has been demonstrated at the contact line when a critical packing fraction is reached regardless of the particle size and initial volume fraction[22]. Alternatively, the stick-slip motion, i.e., the repetition of the pinning and depinning of the contact line, has also been observed in evaporating droplets,[23–26] where the "slip" behavior is a result of the contact angle reaching its static receding value as the droplet evaporates. When the contact line depins, the droplet rapidly reaches its equilibrium contact angle as the contact line "slips" to its next equilibrium position and "sticks" there. As a result of the competition between friction and surface tension forces, the stick-slip motion of the contact line repeats itself until the drop fully evaporates, leaving multi-ring depositions of sessile drops[25,27–30] and capillary bridges,[4,31,32] as well as well-spaced strip patterns in dip coating applications.[5,33]

Particle wettability has been shown to play an important role in determining the deposition morphologies of colloidal drops. Anyfantakis et al.[34] showed that, for microliter sessile drops, both hydrophilic and hydrophobic particles form coffee-ring deposits at low concentrations. At high concentrations, however, the deposition transitions from a ring to a dome-like pattern with increasing particle hydrophobicity, due to enhanced self-assembly of hydrophobic particles forming a connected network that prevents them from being pushed to the drop edge. Alternatively, Shao et al.[35] has shown that copolymer particles that are less hydrophilic form ring patterns whereas more-hydrophilic silica particles yield spoke depositions owing to the increased capillary force with particle wettability, assuming that particles are adsorbed to the drop surface. However, because most colloidal drop deposition studies mainly rely on *post-mortem* analysis, it is still unclear how the particle wettability affects the contact line dynamics as the drop evaporates. This is particularly true for inkjet-printed, pico-liter colloidal drops where the evaporation time scale is much shorter than the particle diffusion time scale for either particle self-assembly or adsorption to drop surface to occur.

In this study, we seek to bridge the gap between the particle wettability and the stick-slip motion of the contact line of inkjet-printed colloidal droplets using *in situ* observation of the evaporation process. High-speed interferometry, combined with *post-mortem* deposition profilometry, is used to obtain the instantaneous contact line motion, contact angle, drop volume, and particle volume fraction. Dilute aqueous inks containing monodispersed 20 nm carboxylate-modified (more hydrophilic) or carboxyl (less hydrophilic) polystyrene particles are used while other parameters are kept the same. The experimentally observed dependence of the stick-slip motion of the contact line on particle wettability is compared with model predictions of the number of particles required to pinning based on a force balance of particles at the contact line. The instantaneous particle deposition rates during the colloidal drop evaporation process for particles of varying wettability are also obtained. Integrating modeling and experiments, we correlate among the particle wettability, contact line motion, and final deposition morphology of inkjet-printed evaporating colloidal drops.

2. Experimental Methods

The custom-built printing setup shown in Figure 1a consists of a piezoelectric drop-on-demand printer synchronized with side-view flash photography to ensure stable droplets jetted from a print head with an orifice diameter of 80 μm (MicroFab MJ-AL-01). The picoliter-sized droplets were formed via a pneumatic control device (MicroFab) and a waveform generator (JetDrive). The side-view imaging of the drop was conducted using a 12× Navitar lens on a SensiCam CCD camera in tandem with a halogen strobe light (PerkinElmer). The lighting, imaging and droplet jetting were synchronized with a delay generator (SRS DG645) to obtain droplets of ≈60 μm diameter. The droplets were printed onto cleaned glass slides (Chemglass) which were also made more hydrophilic by plasma cleaning (2 minutes of air plasma at 18 W and 250 mTorr, Harrick Plasma PDC-32G). The equilibrium contact angle of water on plasma-cleaned glass substrates was measured to be close to 0° from a custom-built goniometer and the LB-ADSA drop analysis plugin of Image J (http://rsbweb.nih.gov/ij/). The relative humidity was controlled using an environmental chamber and the ambient temperature was maintained at 22°C.

The ink was prepared by adding deionized water to 20 nm carboxyl (less hydrophilic, Invitrogen C37261) and carboxylate-modified (more hydrophilic, Invitrogen F8787) polystyrene nanoparticle suspensions to obtain a particle volume fraction of 0.0025. Those nanoparticles are sulfate polystyrene particles, grafted with the carboxyl group. The ionization of the carboxyl group makes it more attracted to water molecules, thus responsible for the change of wettability. Carboxyl polystyrene nanoparticles[36] are charge-stabilized with a very low number of carboxyl groups present on the sulfate PS particle surface. Thus, the equilibrium contact angle for carboxyl PS particles is approximated to be the same as the sulfate PS particle of $\theta \approx 74°$.[37] Whereas, carboxylate-modified polystyrene nanoparticles[36] are produced by copolymerizing carboxylic acid containing polymers grafted onto their already charged surfaces, which results in greater surface charge densities and higher hydrophilicity. The equilibrium contact angle for carboxylate-modified PS particle is approximated as $\theta \approx 34°$ by comparing its surface charge density with existing measurements.[38] Note that these contact angle approximations are also based on the assumption that the particle wettability is not a strong function of the particle size [37,39]. The measured zeta potentials were -68.8 mV for carboxylate-modified particles and -37.4 mV for carboxyl particles using a Zetasizer Nano (Malvern). The water and particle mixtures were then homogenized for 5 minutes in a sonicator (Cole-Parmer 8891) prior to printing.

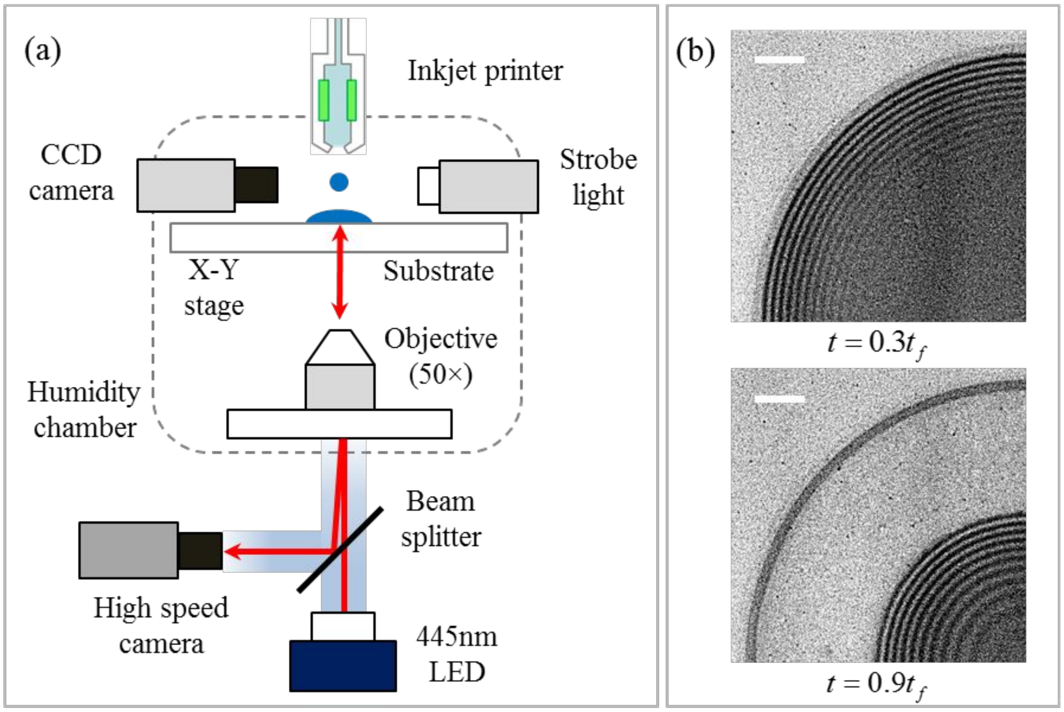


Figure 1: (a) Schematic depiction of the interferometry technique for inkjet-printed drops. The dashed line represents the humidity-controlled chamber (b) Interferometry images of an

evaporating aqueous drop of 113 pL containing 20 nm carboxylate-modified particles at $t = 0.3t_f$ and $t = 0.9t_f$, where t_f is the total evaporation time. The initial particle volume fraction is 0.0025 and the relative humidity of the chamber is 35%. The scale bar represents 20 μm.

The bottom-view interferometry imaging was conducted based on constructive (bright fringes) and destructive (dark fringes) interference resulting from the phase shift between the incident light reflected from the water-air and water-glass interfaces, respectively. The interferometry imaging setup consists of a 50× objective connected to an inverted microscope (Zeiss Axio Observer A1) illuminated by a blue (445 nm) high-powered light-emitting diode (LED) (Thorlabs Solis-445C) and recorded at 10,000 frames per second with a resolution of 0.4 × 0.4 μm per pixel by a high-speed camera (Phantom V711). The captured interferometry images (Figure 1b) were analyzed based on the well-known premise that the fringe-to-fringe spacing correlates to a local drop thickness differential of $\lambda/2$, where λ is the wavelength of the light source. The maximum measurable thickness is a strong function of the coherence of the light source used and for the LED (coherence length of 5.7 μm) used in this study, the maximum measurable thickness was a few micrometers. The minimum measurable thickness depends on the wavelength of the light source and is $\lambda/4 \approx 111$ nm in the present study. With a temporal resolution of 100 μs, the interferometry technique allows for the instantaneous measurement of the drop thickness near the contact line and hence the contact angle from linear fitting of ten nearest data points from the contact line. Once the contact angle is obtained, the full droplet profile is determined by the spherical cap fitting[11], following $z = \sqrt{R^2/\sin^2\Theta - r^2} - R/\tan\Theta$, where z is the local droplet height, R the contact line radius, r the local radius, and Θ the apparent drop contact angle. Note that, in this study, the Bond number $\mathrm{Bo} = \rho g d_0^{\,2}/\gamma < 0.005$ such that the gravitational effect on the drop shape is negligible. Here, ρ is the density of water, g is the gravitational acceleration, d_0 is the drop in-flight diameter, and γ is the surface tension of water. Figure 1b shows the interferometry images of an evaporating aqueous drop containing 0.25% 20nm carboxylate-modified particles at $t = 0.3t_f$ and $t = 0.9t_f$ (t_f the total evaporation time), where well defined fringe patterns were observed close to the contact line. In addition, an optical profilometer (Zygo 7100) was used to analyze the deposition pattern *post-mortem*. As the high-speed interferometry tracked the instantaneous location of the contact line and the droplet shape, for each time frame, the contact line radius and droplet volume can be correlated with the *post-mortem* particle deposition profile at that contact line location. Combining *in situ* drop surface profile and *post-mortem* deposition profilometry thus allows for the determination of the instantaneous particle volume fraction of the remaining colloidal drop and the time-dependent particle deposition rate.

3. Model for the Number of Particles Required to Pinning

To understand the effect of particle wettability on contact line pinning, a force balance analysis is conducted on the particles near the contact line as shown in Figure 2a with the following assumptions:

i) For picoliter-sized droplets, the particle Brownian motions are neglected close to the contact line where the particle Peclet number, $\mathrm{Pe} = 2R_{depo}v_r / D_p \approx 8400$, is large. Here, R_{depo} ≈ 110 µm is the deposition radius of the droplet, v_r ≈ 0.91×10^{-3} m/s is the velocity of the evaporation-driven outflow inside the just-printed sessile drop (evaluated at the contact line using Eq. (3) with $\Theta \approx 6^\circ$ and $z \approx 10\,\mathrm{nm}$), and $D_p = k_B T / 6\pi\eta r_p$ ≈ $2.4\times10^{-11}\ \mathrm{m}^2/s$ is the particle diffusivity in water from the Stokes-Einstein equation,[40] where k_B is the Boltzmann's constant, T is the temperature, η is the dynamic viscosity of water, and r_p is the radius of the particle.

ii) The contact line of the drop is initially pinned and the water-air interface during evaporation is presumably a spherical cap. Gravitational effects are neglected during evaporation since $\mathrm{Bo} = \rho g d_0^2 / \gamma < 0.005$.

iii) The evaporation process is assumed to be limited by vapor diffusion in air where the drop surface is assumed to be in phase equilibrium.[41]

iv) Particles are initially considered to be uniformly distributed and dilute inside the printed drop. The van der Waals and electrostatic interactions between particles in the bulk of the droplet are not considered because the forces acting on one particle by the surrounding particles cancel each other such that the net effect is negligible. The non-DLVO forces acting on the particles are also neglected.

v) The hydrodynamic drag force acting on the particles near the contact line is assumed to be constant considering that the velocity of the evaporation-driven outward flow does not vary significantly near the contact line (e.g., the radial velocity reduces from 0.91×10^{-3} m/s to 0.21×10^{-3} m/s 5 μm away from the contact line). The change in drop viscosity due to particle packing near the contact line is ignored.

vi) The surface tension force is acting on the partially wetted outmost particle of the pinned contact line with an air-water-particle contact angle θ shown in Figure 2b. Monolayer particle assemblies on the substrate are assumed near the contact line for force calculations. In addition, the equilibrium and critical receding contact angles of the particle are assumed to be the same.

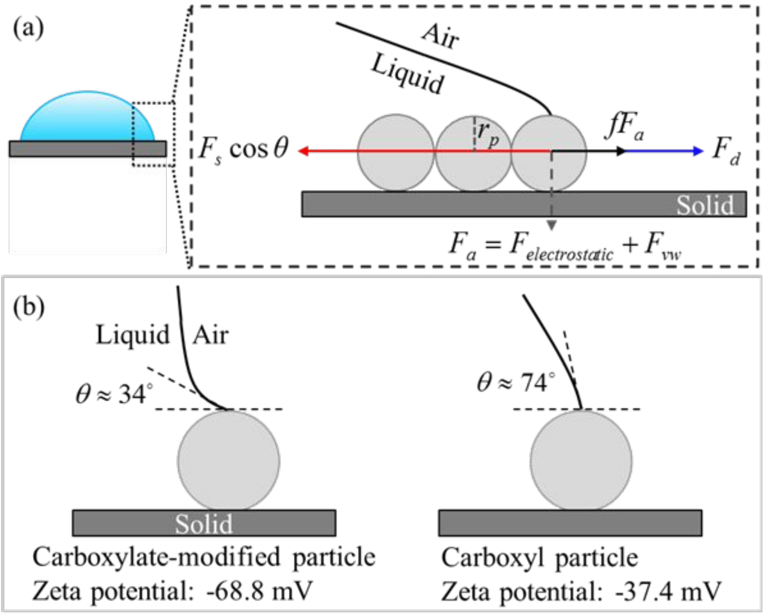


Figure 2. (a) Schematic view of the surface tension (F_s), hydrodynamic drag (F_d), static friction (fF_a), and particle-substrate attraction (F_a) forces acting on particles near the contact line. (b) Schematic of the contact angle (θ) for the carboxylate-modified (more hydrophilic) and carboxyl (less hydrophilic) polystyrene particles at the triple-phase contact line.

As shown in Figure 2a, the horizontal component of the surface tension force acting on the particles near the contact line can be written as $F_s \cos\theta$, where F_s is the water-air surface tension force given as[42]

$$F_s = 2\pi r_p \sigma \tag{1}$$

Here, r_p is the particle radius and σ is the surface tension of the water-air interface.

The horizontal component of the hydrodynamic drag for a stationary particle inside the evaporating drop can be approximated by[42]

$$F_d = 6\pi r_p \eta v_r \tag{2}$$

where η is the dynamic viscosity of water and v_r is the radial velocity of the evaporation-driven outward flow. Following the Hu−Larson model for a diffusion-limited evaporating droplet with a pinned contact line,[43] the radial velocity of the evaporation-driven outflow inside the sessile drop is given by

$$v_r = \left\{ -\frac{3}{8}\frac{1}{\tilde{r}}\left[(1-\tilde{r}^2) - \left(1-\tilde{r}^2\right)^{\Theta/\pi-1/2} \right] - \frac{\tilde{r} z_0^2 \tilde{z}}{2R_{depo}^2}\left[\tilde{J}\left(\frac{1}{2}-\Theta/\pi\right)\left(1-\tilde{r}^2\right)^{\Theta/\pi-3/2} + 1 \right] \right\} \frac{R_{depo}}{t_\mathrm{f}} \tag{3}$$

where $\tilde{r} = r / R_{depo}$ is the dimensionless radius, Θ is the apparent contact angle of the droplet which can be experimentally measured from interferometry, $R_{depo} = \left\{ \pi d_0^3 / \left[3\pi \tan(\Theta/2) \right] \right\}^{1/3}$ is the droplet deposition radius, d_0 is the drop in-flight diameter, $\tilde{z} = z / z_0$ is the dimensionless drop height, z_0 is the initial drop height, $\tilde{J}(\tilde{r})$ is the local evaporation flux and $\tilde{J} = \left(t_f / \rho z_0\right)\left(1-\tilde{r}^2\right)^{\Theta/\pi-1/2}\left(Dc_\mathrm{v}(1-RH)/R_{depo}\right)\left(0.27\Theta^2+1.3\right)[0.6381-0.2239\left(\Theta-4/\pi\right)^2]$ is obtained from curve fitting numerical solutions of an evaporating pinned sessile drop[43]. Here, the total drying time $t_f = \pi\rho R_{depo}^2 \tan(\Theta/2) / \left[8D(1-RH)c_v\right]$[11,17], where D is the diffusivity of water vapor in air, c_v is the saturated vapor concentration, and RH is the relative humidity. The hydrodynamic drag for a stationary particle at the contact line can be evaluated by setting $r = R_{depo} - z/\tan(\Theta/2)$ with $z \approx 10$ nm (the particle radius) and using an experimentally measured drop wetting angle Θ.

The attraction force, F_a, between particles and the substrate can be calculated by[16,42]

$$F_a = F_{VW} + F_{electrostatic} \tag{4}$$

which includes both van der Waals and electrostatic interactions. The van der Waals force between particles and the substrate in a fluid medium is given by[44]

$$F_{VW} = 2nA_{123}r_p^3 / [3Z^2(Z+2r_p)^2] \tag{5}$$

where n is the number of particles near the contact line, Z is the minimum separation distance between the particle and the substrate, and A_{123} is the Hamaker constant where the subscript 1 denotes the particle, 2 is the substrate, and 3 denotes the fluid medium. The electrostatic force between particles and the substrate in a fluid medium can be written as[45]

$$F_{\text{electrostatic}} = -2n\pi r_p \varepsilon\kappa[\varphi_1{}^2 + \varphi_2{}^2 - 2\varphi_1\varphi_2 \exp(\kappa Z)] / [\exp(2\kappa Z) - 1] \qquad (6)$$

where ε is the fluid permittivity, κ is the reciprocal of the Debye length, ϕ_1 is the zeta potential of the particles, and ϕ_2 is the zeta potential of the substrate. The static friction force arises due to this attraction force between particles and substrate can hence be expressed as, fF_a, where f is the friction coefficient that depends on the roughness of the contacting surface.[46,47] For particles of different wettabilities, the friction coefficient is assumed to be the same. In addition, the static friction force and the hydrodynamic drag are assumed to be independent and both contribute to the motion of the particles near the contact line.

Based on the balance of the surface tension, hydrodynamic drag, and static friction forces acting on particles near the contact line, the number of particles required for pinning, n_{pinning}, is hence given by

$$n_{\text{pinning}} = F_s \cos\theta / (F_d + fF_a) \qquad (7)$$

Note that, as shown in Figure 2b, the particle wetting angle θ is about 34° for carboxylate-modified (more hydrophilic) particles and 74° for carboxyl (less hydrophilic) particles.

Using Eqs. (1) - (7) with the property values provided in Table 1, the forces acting on particles near the contact line are estimated and the results are summarized in Table 2. Due to different particle wettabilities, the horizontal component of the surface tension force acting on the particles near the contact line is 1.26×10^{-9} N for carboxyl (less hydrophilic) particles and 3.79×10^{-9} N for carboxylate-modified (more hydrophilic) particles. The hydrodynamic drag force is 1.54×10^{-13} N for both types of particles. The attraction force between particles and the substrate is 3.0×10^{-10} N for carboxyl particles and 2.54×10^{-10} N for carboxylate-modified particles due to their different zeta potentials. For particles of different wettabilities, the change in the denominator of Eq. (7), $F_d + fF_a$, is negligible because the hydrodynamic drag force, F_d, and the friction coefficient, f , are assumed to be independent of the particle wettability and the variation in the attraction force is very small. In addition, the water-air surface tension force, F_s, is independent of the particle wettability. Thus, the ratio of the number of particles required for pinning between the cases of carboxylate-modified (more hydrophilic) to carboxyl (less hydrophilic) particles can be given by, $r_N = \frac{\left(n_{\text{pinning}}\right)_{\text{carboxylate-modified}}}{\left(n_{\text{pinning}}\right)_{\text{carboxyl}}} \approx \frac{\cos\theta_{\text{carboxylate-modified}}}{\cos\theta_{\text{carboxyl}}} \approx 3$. In other words, the number of particles required for pinning near the contact line increases 3 times when the particle wettability increases from wetting angle of 74° to 34° while keeping other parameters the same. The higher requirement for pinning of more hydrophilic particles presented here is consistent with the molecular dynamics simulation results of Li et al.,[48] which showed the hydrophobic particle makes the contact line pinning easier than the hydrophilic one under the same substrate condition.

Table 1. Summary of parameters used in force calculations of evaporating aqueous colloidal drops containing polystyrene nanoparticles printed on glass.

Symbol	Physical parameter	Value	Unit
A_{123}	Hamaker constant between particle and glass in water	3×10^{-20} [45]	J
c_v	Saturated vapor concentration in air	0.0232	kg/m^3
d_0	Drop in-flight diameter	60×10^{-6}	M
r_p	Radius of the particle	10×10^{-9}	M
v_r	Radial velocity of the evaporation-driven flow at the contact line	0.91×10^{-3} (Eq. 3)	m/s
Z	Minimum particle separation distance	0.4×10^{-9} [45]	M
ε	Permittivity of water	7×10^{-10}	F/m
η	Dynamic viscosity of water	0.9	cP
κ	Reciprocal of the Debye length	$(430\times10^{-9})^{-1}$ [45]	m^{-1}
ρ	Density of water	1000	kg/m^3
σ	Surface tension of water	0.072	N/m
ϕ_1	Zeta potential of polystyrene particles	-68.8 (carboxylate-modified) -37.4 (carboxyl)	mV
ϕ_2	Zeta potential of glass	-40 [45]	mV

Table 2. Forces acting on particles near the contact line of an inkjet-printed aqueous colloidal drop containing polystyrene nanoparticles on glass.

Parameters	Carboxyl PS particles	Carboxylate-modified PS particles
$F_s \cos\theta$	1.26×10^{-9} N	3.79×10^{-9} N
F_d	1.54×10^{-13} N	1.54×10^{-13} N
F_a	3.0×10^{-10} N	2.54×10^{-10} N
$r_N = \frac{\left(n_{\text{pinning}}\right)_{\text{carboxylate-modified}}}{\left(n_{\text{pinning}}\right)_{\text{carboxyl}}}$		≈ 3

4. Results

In order to understand the deposition morphologies of nanoparticles with different wettabilities, Figure 3 shows the optical profilometry images of the deposition patterns of inkjet-printed colloidal drops containing 0.25%, 20nm carboxylate-modified (Figure 3a, more hydrophilic) and carboxyl (Figure 3b, less hydrophilic) nanoparticles, respectively, on a plasma-cleaned glass substrate with an in-flight drop diameter of 60 μm at a relative humidity of 35%. As shown in the zoomed-in images on the left, an outmost ring is observed for both cases, but a thicker ring of ≈0.06 μm thick and ≈5.2 μm wide is obtained for the more hydrophilic case (Figure 3a) compared with that of ≈0.02 μm thick and ≈4.4 μm wide for the less hydrophilic case. In addition, at least five well-defined concentric inner rings of ≈0.02 μm thick are observed for the less hydrophilic case (Figure 3b) which transitions into a spider web and foam-like deposition, while a spider web-like deposition is observed right next to the outmost ring for the more hydrophilic case (Figure 3a). As shown in Figure 3, a near hollow center is observed for both cases. Moreover, for the less hydrophilic case shown in Figure 3b, the spacing of the concentric rings decreases from drop edge to the center.

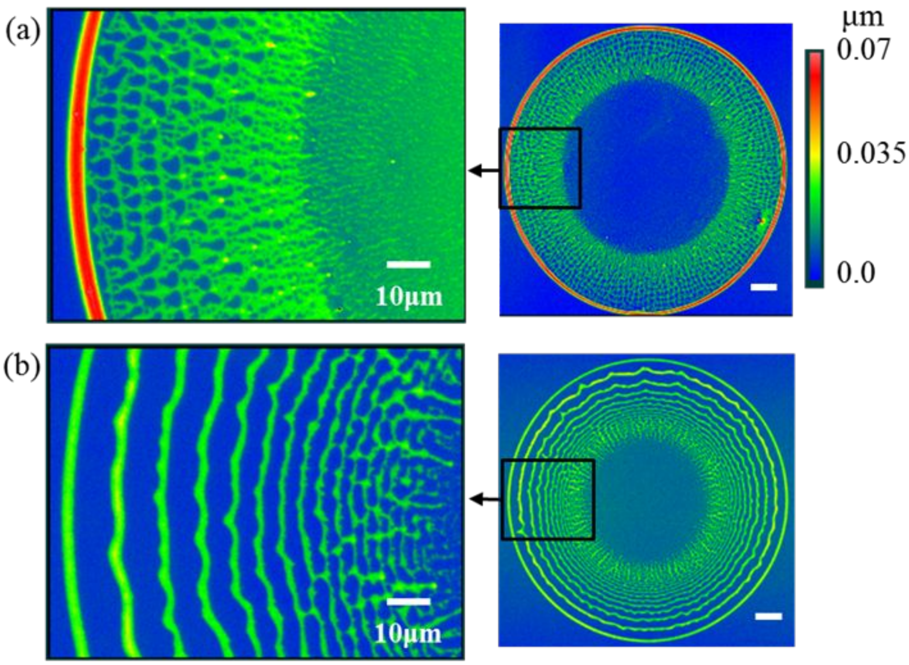


Figure 3. Optical profilometry images of the deposition patterns on a plasma-cleaned glass substrate formed by inkjet-printed aqueous droplets containing (a) 20 nm carboxylate-modified (more hydrophilic) and (b) carboxyl (less hydrophilic) particles. The in-flight drop diameter of 60 μm at a relative humidity of 35%. The particle volume fraction is 0.0025. The scale bar represents 20 μm in the two zoomed-out images of the right column.

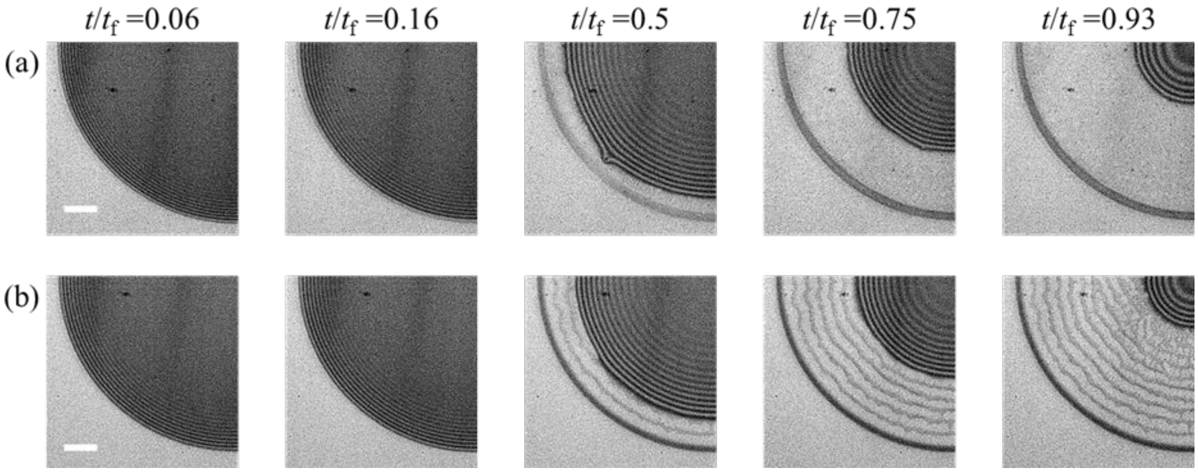


Figure 4. Snapshots of interferometry images of inkjet-printed evaporating aqueous colloidal droplets on a plasma-cleaned glass substrate containing (a) 20 nm carboxylate-modified (more hydrophilic) and (b) carboxyl (less hydrophilic) nanoparticles. The experimental conditions are the same as in Figure 3. The time at which evaporation is completed, t_f, is about 0.7 second, independent of particle wettability.

The interferometry images at $t/t_f = 0.06,\ 0.16,\ 0.5,\ 0.75, \text{ and } 0.93$ for evaporating aqueous colloidal droplets containing 20 nm carboxylate-modified (more hydrophilic) and carboxyl (less hydrophilic) nanoparticles are shown in Figure 4a and b, respectively. The starting time (t = 0) is defined as the inkjet-printed drop touches the substrate and the time at which evaporation is completed, t_f, is about 0.7 second, independent of the particle wettability. Thus, the particle wettability does not have a noticeable influence on the evaporation rate of the droplets. Due to the highly symmetric nature of the deposition process, only a quarter of the drop is shown. For both cases, when the contact line is pinned between $t/t_f = 0.06$ and 0.16, the fringe spacing near the contact line slightly increases, which corresponds to a decrease in the local drop thickness and hence a decreaing contact angle. As the drop continues to evaporate, the contact line recedes from $t/t_f = 0.16$ to $0.5,\ 0.75, \text{ and } 0.93$, leaving behind a single ring for the more hydrophilic case but at least six well-defined concentric rings (including the outmost ring) for the less hydrophilic case. Comparing interferometry images of the same time frames, the contact line moves slower to the drop center for the more hydrophilic case where the fringe spacings are found to be slightly larger, indicating a smaller contact angle as compared to the less hydrophilic case. These *in situ* fringe patterns shown in Figure 4 provide the instantaneous drop shape and direct evidence of how the deposition patterns are formed.

To understand the contact line dynamics of evaporating drops containing carboxylate-modified (more hydrophilic) and carboxyl (less hydrophilic) nanoparticles, Figure 5a shows the normalized instantaneous drop radius, r/r_0, as a function of the normalized time, t/t_f, measured from the bottom-view images. For both cases, after the drop is in contact with the substrate at t = 0, the drop quickly spreads until it reaches the maximum diameter at around $t/t_f = 0.06$. The contact line is then pinned until $t/t_f = 0.33$ for carboxyl (less hydrophilic) particles and $t/t_f = 0.39$ for carboxylate-modified (more hydrophilic) particles. As shown in Figure 5a, five noticeable stick-slip cycles, which correspond to the number of inner rings, are found for carboxyl particles from $t/t_f = 0.33$ to 0.72 with longer stick time in the range of $0.047 - 0.070t_f$ as compared with the slip time of $0.010 - 0.025t_f$. Similar stick-slip motions of the contact line have been observed for evaporation of millimeter-sized drops for copolymer (particle contact angle, θ ≈ 70°) and $\mathrm{TiO_2}$ particles.[35,49] Unlike the carboxyl particles, continuous receding of the contact line has been observed for the carboxylate-modified particle case once the contact line depins from the outmost ring. As shown in Figure 5a, the contact line recedes slower for the carboxylate-modified particle case, possibly caused by the continuous deposition of particles (as shown in Figure 3) slowing down the contact line speed. The experiments thus demonstrate the dependence of contact line dynamics on particle wettability.

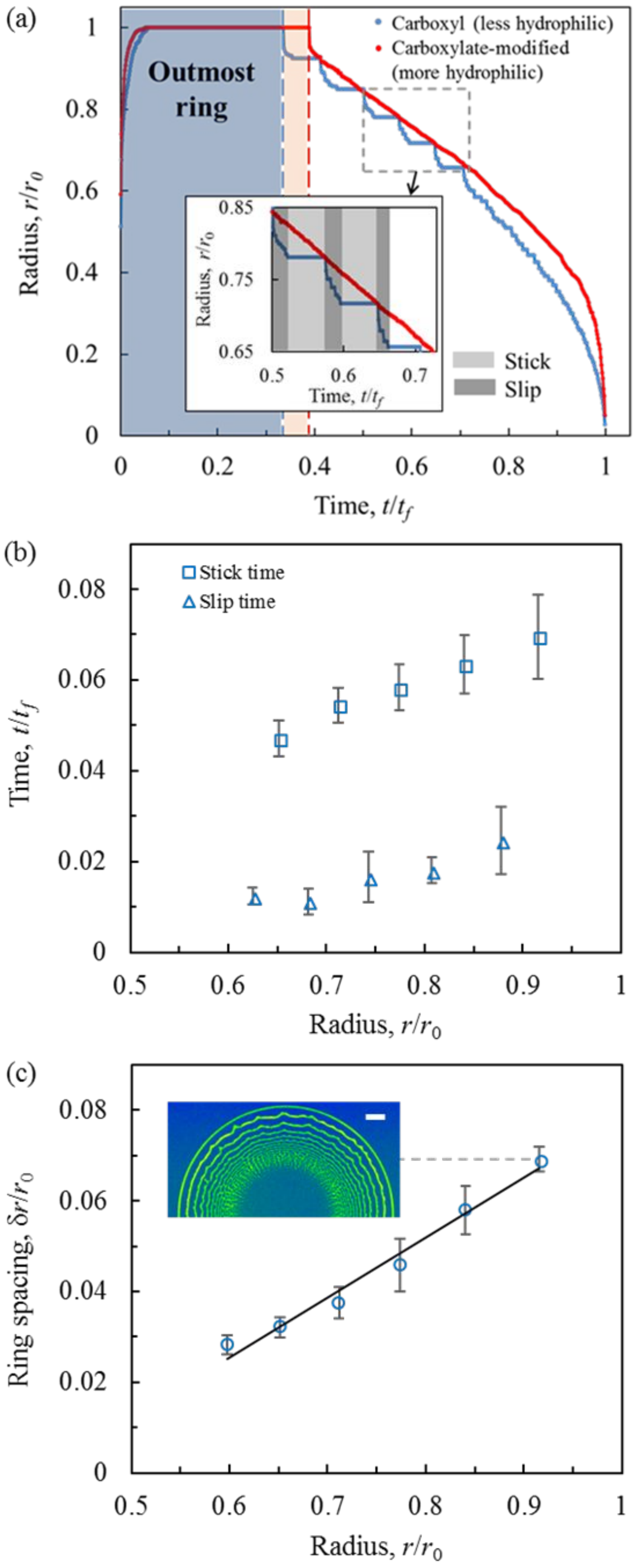

(a)
Outmost ring
Carboxyl (less hydrophilic)
Carboxylate-modified (more hydrophilic)
Radius, r/r_0
Time, t/t_f
0
0.2
0.4
0.6
0.8
1
0.85
0.75
0.65
0.5
0.7
Stick
Slip
(b)
Stick time
Slip time
Time, t/t_f
Radius, r/r_0
0
0.02
0.04
0.06
0.08
0.5
0.6
0.7
0.8
0.9
1
(c)
Ring spacing, $\delta r/r_0$
Radius, r/r_0

Figure 5. (a) Normalized drop radius, r/r_0, as a function of the normalized time, t/t_f, measured from bottom-view images for 20 nm carboxyl (blue) and carboxylate-modified (red) particles, respectively, with the inset showing zoomed-in views of the stick and slip motions of the contact line. (b) Normalized stick (blue squares) and slip (blue triangles) times, t/t_f, as a function of the normalized drop radius, r/r_0, for 20 nm carboxyl particles. (c) Normalized ring spacing, $\delta r/r_0$, as a function of the normalized drop radius, r/r_0, for 20 nm carboxyl particles. The scale bar represents 20 μm. Error bars are obtained on the basis of three independent experiments. The outmost ring is not included in (b) and (c). The experimental conditions are the same as in Figure 3.

To better understand the stick and slip behaviors of the contact line for colloidal drops containing carboxyl (less hydrophilic) particles, Figure 5b shows the normalized stick and slip time as a function of the normalized drop radius, r/r_0, where the corresponding drop radius for the slip time is the average between two consecutive pinned positions of the contact line. A total of five stick-slip cycles are observed, where the stick time is found to be ~3-4 times longer than the slip time, both of which decrease as the drop radius decreases. Figure 5c shows the normalized ring spacing, $\delta r/r_0$, versus the normalized drop radius, r/r_0, for carboxyl (less hydrophilic) particles, indicating the ring spacing decreases from the drop edge to the center, in line with previous observations.[4,27] Good linearity is obtained for experimentally fitted $\delta r \sim r$, consistent with the model prediction[27] assuming a drop of spherical-cap shape before and after a slip motion on a hydrophilic substrate with negligible evaporation during slip.

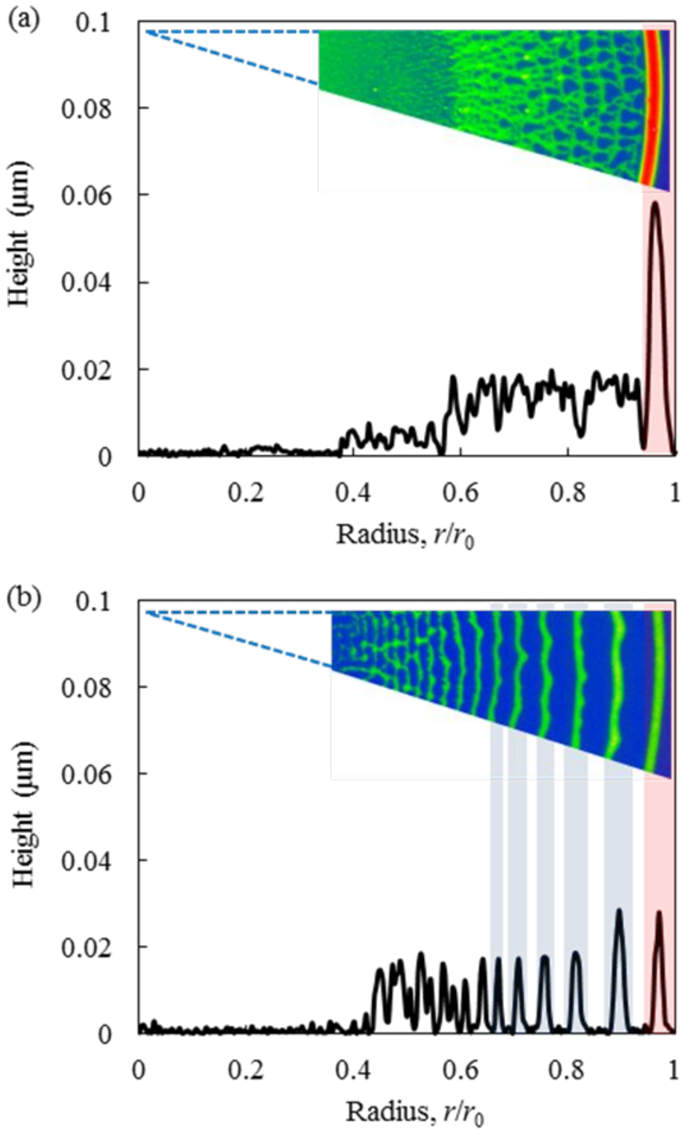


Figure 6. Deposition profile as a function of the normalized drop radius, r/r_0, on a plasma-cleaned glass substrate formed by inkjet-printed aqueous droplets containing 20 nm (a) carboxylate-modified (more hydrophilic) and (b) carboxyl (less hydrophilic) particles. The experimental conditions are the same as in Figure 3.

To quantify the deposition morphology shown in Figure 3, Figure 6 shows the deposition profiles of inkjet-printed aqueous colloidal droplets containing 20nm carboxylate-modified (more hydrophilic, Figure 6a) and carboxyl particles (less hydrophilic, Figure 6b) as a function of the normalized drop radius, r/r_0, on a plasma-cleaned glass substrate obtained from optical profilometry. For carboxylate-modified particles (Figure 6a), about 34.1% of the particles are deposited in the outmost ring. While for carboxyl particles (Figure 6b), the outmost ring contains about 16.5% of the particles and 16.0%, 9.7%, 7.0%, 6.7%, and 6.5% of particles for the second, third, fourth, fifth, and sixth rings, respectively. Hence, the experimentally determined number of particles in the outmost ring is about two times higher for carboxylate-modified than carboxyl particles.

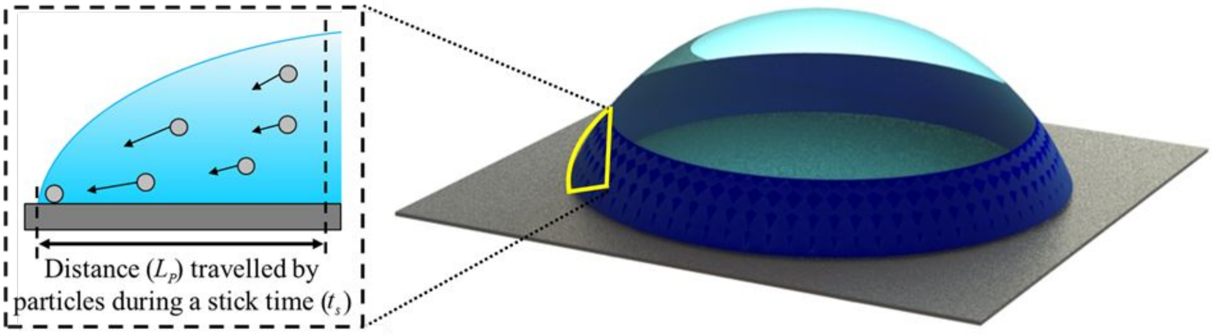


Figure 7. Schematic showing the drop wedge within distance, L_p, to the contact line. Particles in this region can be advected to the contact line during the stick time.

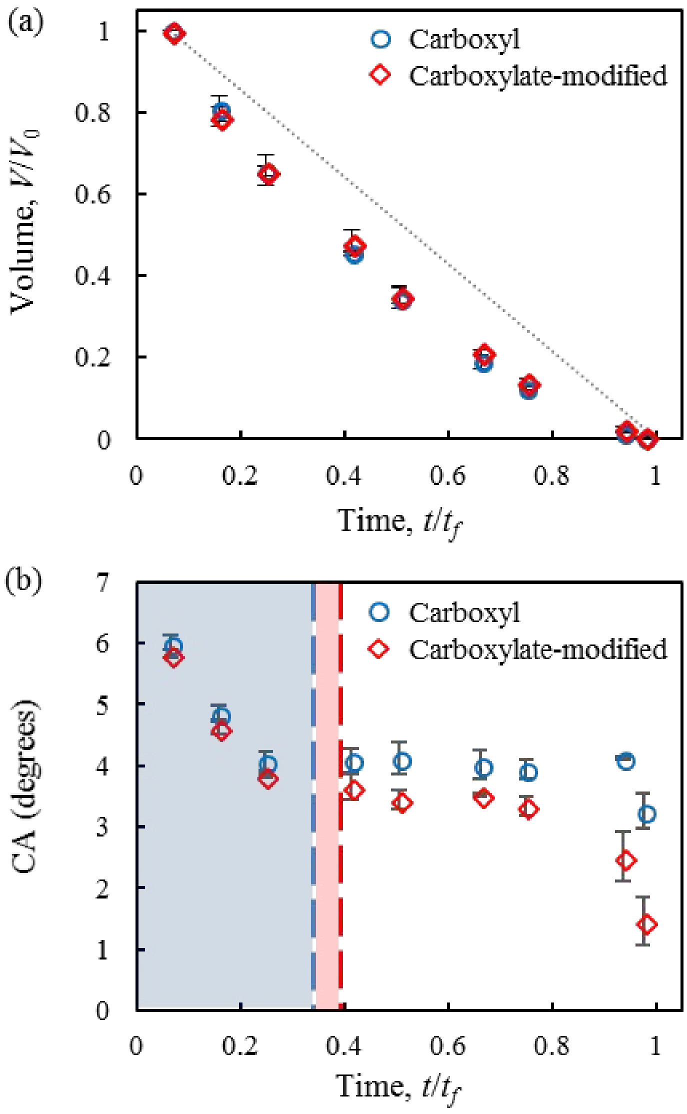
To better understand why the stick-slip motion of the contact line is observed for carboxyl (less hydrophilic) particles while the contact line continues to recede for carboxylate-modified (more hydrophilic) particles, the number of particles accumulated at the contact line during the experimentally measured stick time is determined. As shown in Figure 7, when the contact line is pinned during the stick time t_s, the maximum distance travelled by the particles that finally accumulate at the contact line can be determined by $L_p = \int_0^{t_s} v_r dt$, where v_r is the radial velocity of the particles determined by Eq. (3). Here, in the v_r calculations, we assume that the particles are flow tracers, the drop contact angle is the average value during the entire stick time, the radial position r of the particle changes with time, and the height position z is set to be the particle radius. The number of the particles accumulated at the contact line can then be determined from the volume of the drop wedge within distance L_p to the contact line and assuming particles are uniformly distributed at 0.0025 volume fraction at the beginning of the stick time. Here, the volume of the drop wedge can be calculated by assuming a drop of a spherical-cap shape with a contact angle obtained from interferometry measurement, following

$$\begin{aligned} V_{wedge} &= \frac{\pi}{2}\tan(\Theta/2)R_{depo}^{3} - \pi L_P \tan\Theta (R_{depo} - L_P)^2 \\ &\quad - \frac{\pi}{2}\tan\left[\sin^{-1}((R_{depo} - L_P)/(R_{depo}/\sin\Theta))/2\right](R_{depo} - L_P)^3 \end{aligned} \tag{8}$$

Note that Θ is the apparent drop contact angle, different from the particle wetting angle θ. This yields 9.21% of the particles available near the contact line for the outmost ring, and 1.47%, 1.33% and 1.24% for the second, third, and forth rings, respectively for carboxyl (less hydrophilic) particles. Instead, about 13.6% of the carboxylate-modified (more hydrophilic) particles available near the contact line for the outmost ring, 1.5 times higher than that of carboxyl (less hydrophilic) particles, in qualitative agreement with the 2.1 times obtained experimentally. Meanwhile, for the carboxylate-modified (more hydrophilic) particles, after the outmost ring and assuming the same stick time as that of the carboxyl (less hydrophilic) particles, results in 1.51%, 1.49% and 1.47% of particles available near the contact line for possible pinning during the second, third, and fourth stick time.

On the other hand, Eq. (7) predicts the number of particles, $n_{pinning}$, required for pinning. The total number of particles required for pinning along the periphery of the drop contact line can be estimated by using $N_{pinning} = \left(2\pi R_{depo} n_{pinning}\right) / \left(2r_p\right)$, where R_{depo} is the instantaneous drop deposition radius and r_p is the particle radius. This allows one to compare the number of particles available and the number of particles required to pinning. If the number of particles required to pinning is smaller than particles available, the contact line pins and particles form a ring and vice versa. For example, for carboxyl (less hydrophilic) particles, the number of particles required to pinning is always smaller than particles available for any friction coefficient $f > 0.13$, which results in a pinned contact line. Whereas, for carboxylate-modified (more hydrophilic) particles, the number of particles required to pinning is always larger than particles available when $f < 0.46$, resulting in continuous receding of the contact line. In other words, for the range of friction coefficient, $0.13 < f < 0.46$, the model agrees well with the experimental observations, i.e., the stick-slip motion of the contact line and multi-ring deposition for the carboxyl particle case whereas the continuous contact line receding for carboxylate-modified particles.

Figure 8a-d show the evolution of the drop volume, contact angle, particle number, and particle volume fraction of the evaporating colloidal drops containing carboxylate-modified (more hydrophilic) and carboxyl (less hydrophilic) particles, respectively. The instantaneous drop volume does not show observable dependence on the particle wettability, similar to that observed by Anyfantakis et al.[34] Compared with the dotted linear line that starts at the end of spreading at ~ $0.06t_f$ and ends when the drop fully evaporates at t_f, the evaporation is faster in the first half of the time but slows down in the second half, slightly different from the linear dependence of time as observed by others.[49,50] Figure 8b shows that the contact angle initially starts at about 6° and decreases to about 4° for both cases during the constant contact area mode of evaporation when the contact line is pinned. The contact angle of the drop remains about 4° during the constant contact angle mode of evaporation before it decreases again during the final stage of evaporation where both the contact line and contact angle decrease. Changes of the contact angle during the stick-slip motion of the contact line (i.e., $t/t_f = 0.33$ to 0.72) for carboxyl particles are not observable probably due to a very hydrophilic substrate where the contact angle may vary slightly within the error bars shown in Figure 8b. During the entire evaporation, the contact angle for the carboxyl particle case is larger than that of carboxylate-modified particles.



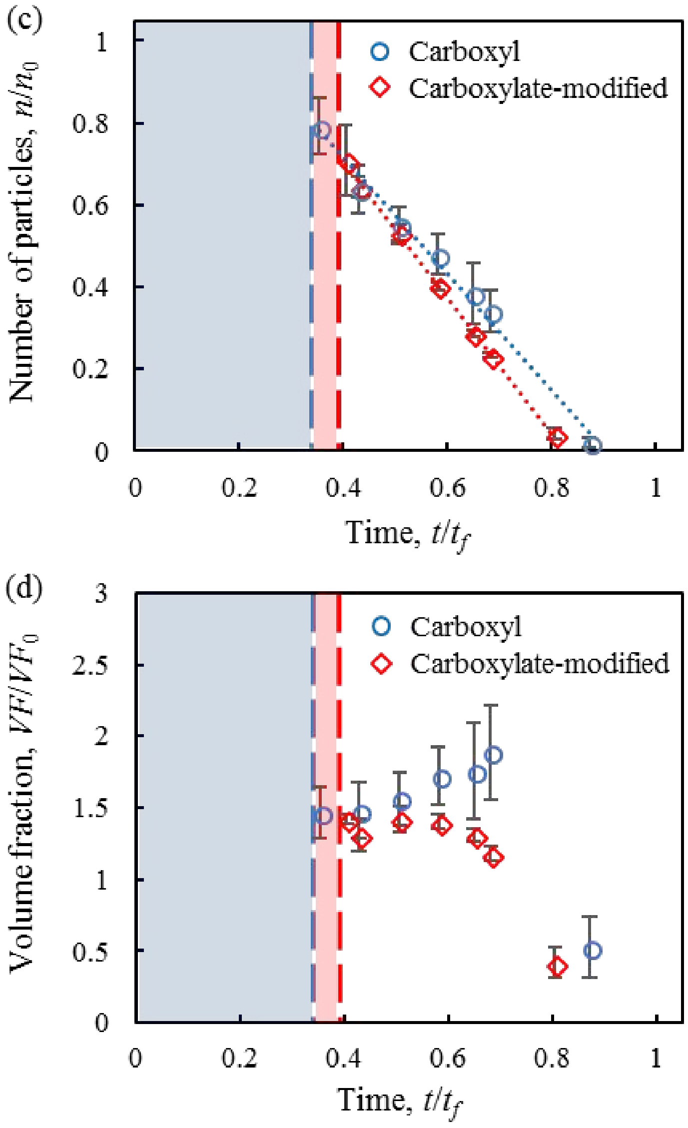


Figure 8. Comparison of (a) the normalized drop volume, V/V_0, (b) the contact angle, (c) the normalized particle number, n/n_0, and (d) the normalized particle volume fraction, VF/VF_0, as a function of the normalized time, t/t_f, for drops containing 20 nm carboxylate-modified (more hydrophilic) and carboxyl (less hydrophilic) particles on a plasma-cleaned glass. The experimental conditions are the same as in Figure 3. Error bars are obtained on the basis of three independent experiments. The blue dashed line represents the experimentally determined time to form the outmost ring for carboxyl particles and the red dashed line indicates the carboxylate-modified particles.

The number of particles remained in the drop is then calculated from subtracting the particles already deposited by the time, t/t_f, from the total number of particles based on *post-mortem* optical profilometry. As shown in Figure 8c, the number of particles remained in the drop decreases linearly with time after the outmost ring for both carboxylate-modified (more hydrophilic) and carboxyl (less hydrophilic) particles, indicating constant particle deposition rates. In addition, a larger slope or a faster deposition rate is found for carboxylate-modified particles as compared to carboxyl ones, mainly due to continuous deposition of particles as the contact line recedes. Moreover, more than 98% of the carboxylate-modified particles are deposited by $t/t_f = 0.80$ and by $t/t_f = 0.88$ for carboxyl particles, leaving near hollow deposition centers consistent with previously shown in Figure 6. Figure 8d shows the instantaneous particle volume fraction of the remaining drop calculated from the remaining deposition volume, based on optical profilometry, divided by the remaining drop volume. It is shown that, the particle volume fraction of the remaining drop first increases and then decreases with time for carboxyl particles, whereas for carboxylate-modified particles the particle volume fraction monotonically decreases. After the outmost ring, the instantaneous particle volume fraction for carboxylate-modified (more hydrophilic) particles is always smaller than that of carboxyl (less hydrophilic) particles. However, more particles are required to pin the contact line for carboxylate-modified (more hydrophilic) particles based on Eq. (7), which further explains why the stick-slip motion does not occur for more hydrophilic particles.

5. Conclusions

In this work, using combined *in situ* interferometry and *post-mortem* profilometry of inkjet-printed colloidal droplets, the effects of particle wettability on contact line dynamics and deposition patterns are examined. The stick-slip behavior of the contact line and the multi-ring deposition are observed only for colloidal drops containing carboxyl (less hydrophilic) particles where both the stick time and the ring spacing are proportional to the drop radius. A model is developed for the number of particles required for pinning based on the force balance of particles at the contact line. The number of particles required to pinning increases three-fold when the particle wettability increases from $\theta \approx 74°$ to $\theta \approx 34°$. After the outmost ring, the number of particles required to pinning is compared against the number of particles accumulated at the contact line during the stick time, resulting in enough carboxyl particles but not enough carboxylate-modified particles available for pinning due to their higher surface tension component which in turn leads to continuous receding of the contact line over the deposited particles for the carboxylate-modified particle case. The results also show that the particle deposition rate is lower for carboxyl (less hydrophilic) as compared to carboxylate-modified (more hydrophilic) particles. The instantaneous particle volume fraction varies during drop evaporation and depends on the particle wettability. These findings will assist in better understanding of materials printing processes for better control of deposition patterns.

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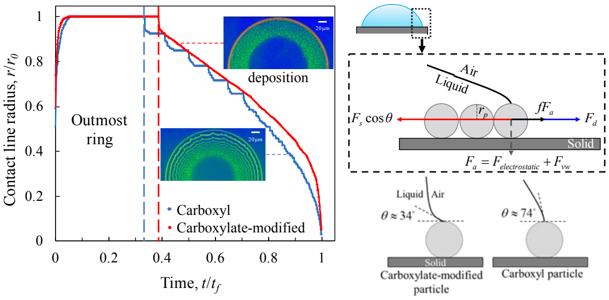

Contact line dynamics and deposition pattern of colloidal drop are strong functions of the particle wettability.