Beyond Coffee Rings: Drying Drops of Colloidal Dispersions on Inclined Substrates

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ABSTRACT: The patterns resulting from drying particle-laden sessile drops (for example, coffee rings, where the particles are concentrated more at the edge, and their complete suppression, where the particles are uniformly distributed throughout the pattern) have been well studied for more than two decades. For the ubiquitous instance of occurrence of drying of drops containing nonvolatile species (either dissolved or dispersed) on substrates oriented at different angles with respect to gravity, the investigation of resulting evaporative patterns has not received much attention. This mini-review addresses the need to investigate the drying of drops residing on inclined surfaces and highlights recent advances in this field.

1. INTRODUCTION

The controlled drying of drops containing dispersed (for example, colloids, nanoparticles, polymers, proteins, DNA, cells, bacteria, and mixtures of two or more constituents) or dissolved (for example, symmetric and asymmetric electrolytes) species is a simple, inexpensive, and widely researched method that facilitates the deposition of any solute of interest in solid surfaces.1 The drying of colloidal and nanoparticle dispersion drops placed on top of horizontal rigid substrates has received considerable attention because it involves transport processes of various time and length scales as well as intriguing physics.2,3 The drying of particle-laden drops is also of relevance to several technological applications such as conventional and circuit board printing and spray coatings leading to functional surfaces. When the solvent from ink drops produced in printing (or other processes involving drops) evaporates, a residue of the solids is left on the substrate on which they reside. Therefore, the study of drop evaporation has generated enormous interest, with the primary goal being the ability to control the spatial distribution of solids in the dried deposits.1,4,5

The first evidence of the nonuniform distribution of particles in the deposits left when particle-laden drops are dried comes from the experimental work of El Bediwi and co-workers.6 The deposits left after the complete evaporation of water from aqueous dispersions of latex particles dried on four different substrates showed a higher density of particles at the boundary with few or almost no particles in the interior. However, it is the work of Deegan et al.2 which provided the first quantitative analysis of the physics of formation of such patterns. The characteristic feature of these patterns is the accumulation of a large concentration of particles at the edge. Such deposits are popularly called coffee rings or coffee stains because they resemble the patterns formed when water evaporates from coffee spills on cups, saucers, tables, and other surfaces. The influential work of Deegan et al.2 paved the way for the development of theoretical, experimental, and simulation methods not restricted only to understanding coffee-ring formation but also to unearthing the particle deposition physics when dispersions are dried in various configurations and geometries.3 Although the deposition of colloids from a drying particle-laden drop in the sessile drop configuration appears to be the most studied, in most practical applications drops dry on substrates that are oriented at an angle with respect to gravity.7 Surprisingly, the physics of deposition of particles and other solutes when drops in such configurations are dried has received very little attention. The gravitational force on the particles in the drop as well as drop deformation due to gravity can influence the evaporation kinetics, transport of particles, and hence morphology of the deposit patterns. In this mini-review, the contrasting deposit patterns obtained from particle-laden drops dried in sessile and pendant configurations and those residing on a vertical substrate are discussed.

This review is laid out as follows. First, in sections 2 and 3 we discuss the effect of gravity on drop shapes and the methods used to characterize gravity-deformed drops. Evaporating drops residing on inclined surfaces (section 4) and patterns formed...
from drying these drops (section 5) are then discussed. Finally, we conclude the review by summarizing the current status and discussing the need for further developments in the field.

2. DROPS ON SURFACES

A drop placed on a completely wetting substrate spreads as a thin liquid film. On the other hand, a drop on a completely nonwetting surface assumes the shape of a sphere. However, in most practical applications, drops deposited on solid surfaces have a three-phase contact angle, \( \theta \), lying between 0 and 180°. The three-phase contact angle (\( \theta \)) is defined as the angle that the tangent (drawn at the three-phase contact point to the drop surface) makes with the solid substrate. A drop residing on top of a horizontal substrate is called a sessile drop. A drop hanging or suspended from a horizontal substrate is called a pendant drop. Spraying, coating, and printing are some examples of practical relevance that involve the deposition of drops on surfaces. Note that depending on the specific application, the wettability of the substrates on which the drops reside, quantified by measuring the contact angle of drops on the solid substrates, may be different. Most often, the drops are sprayed on substrates that are oriented at an angle with respect to gravity. A common example of this comes about in the agricultural sector, where the drops containing nutrients or other chemical species land on leaves of different wettability (depending on the crop type and top/bottom of the leaf surface) orientated at various angles with respect to gravity.

In several applications mentioned above, the drops essentially are multicomponent. That is, they contain a carrier liquid and one or more constituents that are either dissolved or dispersed. When the carrier liquid in these drops completely evaporates, a residue of the nonvolatile matter is left behind on the solid substrates. Such deposits are called the drying or evaporative patterns, and the spatial distribution of the nonvolatile species is influenced by several parameters such as the evaporation rate, the presence of additives such as salt and surfactant, colloidal interactions, the particle shape and concentration, and substrate properties.

3. DROPS ON SURFACES: ROLE OF GRAVITY

A common feature of drops in sessile and pendant configurations is their axisymmetry about the direction of gravity. Characteristics such as the spherical cap shape and axisymmetric nature of drops in sessile or pendant configurations continue to persist as long as the drop volume is on the order of pico-, nano-, or a few microliters. When the drop volume is increased, gravity will deform the drop, and the shape will deviate from the spherical cap; however, the axisymmetry is still preserved. The deviation of the drop shape from a spherical cap can be determined from a hydrostatic pressure balance

\[
\sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) - \frac{2\sigma}{R_o} = \mu g z
\]

(1)

where \( R_1 \) and \( R_2 \) are the two principal radii of curvature measured at any height \( z \) measured from a reference point (\( z = 0 \)) at which the radius of curvature is \( R_o \). Also, \( g \) is the acceleration due to gravity, \( \rho \) is the liquid density, and \( \sigma \) is the interfacial tension between the drop and the surrounding air. The above expression describes the equality of pressure change inside the drop due to difference in interface curvature between any two points \( z = 0 \) and \( z = z \) (LHS of eq 1) and the gravitational head (RHS of eq 1) between these two points for maintaining a static equilibrium.

It is interesting to note that the hydrostatic pressure increases from apex to the base when the drops are in sessile configuration. On the contrary, the hydrostatic pressure decreases from apex to the base in the case of drops in pendant configuration. The relative importance of gravity, which acts to deform the drop and the surface tension force that favors reduction in the surface free energy and hence oppose this deformation is quantified by Bond number. The Bond number (\( B_o \)), defined as the ratio of gravitational force to surface tension force, is given by \( R_o^2 \mu g/\sigma \), where \( R_o \) is the characteristic size of the drop. For aqueous drops of 0.5 \( \mu L \) (\( \approx 0.0005 \) m equivalent spherical radius) to 10 \( \mu L \) (\( \approx 0.0013 \) m equivalent spherical radius), typically used in drying drop problems, the Bond number (\( B_o \)) takes a value between \( 0.03 \) and \( 0.23 \). While \( B_o = 0.23 \) indicates that gravity is 0.23 times as important as surface tension, a 10 \( \mu L \) drop is sufficiently deformed by gravity. This statement can be made because, in measuring the interfacial tension of liquids by pendant drop method, which exploits the principle of drop shape analysis, typical volume of liquids used is \( \approx 10 \) \( \mu L \) or higher. Such drops are sufficiently deformed, a feature that enables the direct determination of surface tension by a balance of surface tension and gravitational forces (eq 1). Since the total surface area available for evaporation and the rate of evaporation can change drastically when the drops are deformed, this is expected to influence the patterns formed by drying deformed particle-laden drops, which will be further elaborated in section 4. However, the gravity driven deformation of drops either in sessile or pendant drop mode becomes negligible when the drops reside on substrates on which they exhibit low contact angle. As stated earlier, the orientation of the substrates on which drops reside \( \phi \) can vary from 0° to 180°. In such cases, the shape symmetry is clearly broken, and such drops in most cases are not axisymmetric. The extent of asymmetry can be quantified from the difference in the three-phase contact angle of the drop measured at the front or lower end \( \theta \) and at the rear or upper end \( \theta_o \), commonly called the contact angle hysteresis in the studies of drops on inclined surfaces. The measurement of contact angle hysteresis is one of the most simple ways to ascertain if the drops are deformed. The contact angle hysteresis and the role of gravity on the drop are well studied however, not in the context of drying drop problems. The gravity-driven deformation of the shape of drops and hence the deviation from spherical shape becomes prominent when drops of large volume are considered and is amplified significantly (i.e., the asymmetric shape of the drop becomes macroscopically visible when the drops are placed on high-contact-angle substrates). As an example, a water drop with volume of as small as 8 \( \mu L \) on a near neutrally wetting \( (\theta = 91 \pm 1^\circ) \) vertical surface \( (\phi = 90^\circ) \) presented in Figure 1 clearly shows that drop deformation on high-contact-angle surfaces is significant even when \( B_o = 0.21 \).

Another possible way to characterize deformed drops is in terms of sphericity, a concept which is well established in particle technology as a measure of the deviation of particle shape from a perfect sphere. Sphericity \( (\Phi_{sph}) \) in the context of deformed drop characterization can be defined as the liquid–air surface area of the drop calculated in the absence of gravity \( (\gamma = 0) \) and substrate orientation \( (\phi = 0) \), \( S_{\text{spherical cap}} \) divided by the liquid–air surface area of the deformed drop, \( S_{\text{deformed}} \):

\[
\Phi_{\text{sph}} = \frac{S_{\text{spherical cap}}}{S_{\text{deformed}}}
\]

(2)
Since both the surface area of a sphere and that of a spherical cap are minimized for a given volume, $\Phi_{\text{drop}}$ varies between 0 and 1. Therefore, $\Phi_{\text{drop}} = 1$ for a drop that is not deformed and $\Phi_{\text{drop}} \to 0$ for a drop that is deformed significantly (under the action of gravity). For drops residing on a surface of any wettability (i.e., fixed $\theta$), $\Phi_{\text{drop}}$ will be lowest when $\phi = 90^\circ$. Moreover, $\Phi_{\text{drop}} \to 1$ when $\theta \to 0$ or $\phi \to 0$ and $B_o \to 0$. $\Phi_{\text{drop}}$ can also be defined on the basis of the total surface area of the drop (surface area of the liquid-air surface and area of the base). Surprisingly, there have been no reports on the consequence of deformation of particle-laden drops on the evaporation-driven patterning of colloids possibly because a majority of the drop drying experiments have been carried out on a drop-substrate combination where $\theta < 20^\circ$, except for some recent studies, as elaborated on in the following sections.

4. EVAPORATING DROPS ON INCLINED SURFACES

One of the simplest ways to understand the influence of substrate orientation and thus gravity is to analyze the total time taken for the complete evaporation of the solvent from the drying dispersion drop. The total drying time is directly proportional to (i) the total drop surface area which is available for evaporation and (ii) the evaporative flux on the surface. However, both of these quantities are strongly dependent on the drop shape, subtle changes in which can occur when the drops are residing on inclined surfaces, as described below.

Sessile drops under negligible gravity, $B_o \ll 1$, take the shape of a spherical cap. The dimensions of the spherical cap (i.e., height and contact diameter) depend solely on the contact angle of the drop and therefore the total surface area available for evaporation, which is the surface area of the spherical cap ($S_{\text{spherical cap}}$). The second factor, namely, the evaporative flux ($J$) on the spherical cap surface, is nonuniform. The evaporative flux for a drop drying on a hydrophilic substrate is minimum at the drop apex and increases toward the edge with the maximum being at the contact line. Thus, the total fluid volume evaporated per unit time from this spherical cap is given as $\int_{S_{\text{spherical cap}}} J \, dS$. Hence the total evaporation time is a function of the drop shape even for sessile drops with $B_o \ll 1$. Hu and Larson\(^{13}\) have calculated the approximate drying rate, expressed as the time rate of change of drop mass ($m$) as $\frac{dm}{dt} = -eR_cD_v(1 - H)(0.27\theta^2 + 1.30)$, where $R_c$ is the radius of the contact line, $c_i$ is the saturated water vapor concentration, and $H$ is the relative humidity. For small contact angles, $\theta < 40^\circ$, it has been found theoretically and experimentally that the rate of change of mass of the evaporating drop does not change significantly with time. In other words, the total lifetime or total evaporation time for a 1 $\mu$L drop will be approximately the same when the sessile drops are dried on substrates of different wettability as long as $\theta < 40^\circ$.

The drop shapes deviate from the spherical cap when gravity effects are not negligible, when $B_o$ is $O(1)$ or higher. On orientated substrates, the drops are not even axisymmetric. Thus, the two factors mentioned above, namely, the total surface area available for evaporation and the evaporative flux, will be different for drops residing on substrates oriented at an angle with respect to gravity which can lead to nontrivial evaporation kinetics. While detailed theoretical estimates are not available, experiments show interesting consequences when drops are dried on substrates oriented at an angle with respect to gravity even when $B_o$ is $O(1)$. The lifetime ($t_F$) of an 8 $\mu$L pure water drop (which corresponds to Bond number $B_o = 0.21$), dried on substrates at different substrate inclination angles ($\phi$) varying from 0 to $\pi$ in steps of $\pi/4$ and obtained\(^{16}\) by measuring the mass of the evaporating drop using an electronic balance, is shown in Figure 2. Figure 2(a) shows that the time in which the mass of the drop decreases to zero as a result of the evaporation of water changing significantly depending on $\phi$. Compared to the drops dried in sessile drop mode ($\phi = 0$), the drops oriented at $\phi = \pi/4$ are observed to dry slowly. With further increases in the orientation of the drop to $\phi = \pi/2$ (i.e., for the drop dried on a vertically inclined substrate), the evaporation time is found to be the highest. That is, 8 $\mu$L pure water drops dried on vertical substrates ($\phi = \pi/2$) take the longest time to evaporate. As the drop orientation is changed further from $\phi = \pi/2$ to $\pi$, the lifetime of the drop decreases monotonically. Therefore, in general, the rate of evaporation of drops residing on inclined surfaces is observed to be slower, with the drops inclined at $\phi = \pi/2$ taking the longest time to dry. The contact angle hysteresis measured at initial time $t = 0$ is shown to follow a trend similar to the droplet lifetime as the substrate inclination is varied from 0 to $\pi$\(^{16}\) (Figure 2(b)).

Another important way in which gravity affects the evaporation dynamics of a drop is by altering the pinning–depinning dynamics of the contact line.\(^{14}\) On an inclined surface, the contact angle on the lower side is larger than the contact angle on the upper side ($\theta_l > \theta_u$) for a gravity-deformed drop. Therefore, the evaporative flux which decreases with increasing contact angle is larger near the upper contact line compared to that near the lower contact line. Consequently, the larger loss of solvent will result in a faster change in the upper contact angle (i.e, $\frac{d\theta}{dt} > \frac{d\theta}{dt}$ for $\theta_l > \theta_u$). This change also results

![Figure 1. Shape of an 8 $\mu$L water drop on a near neutrally wetting ($\theta = 90^\circ$) vertical surface. Figure courtesy of Kim et al.\(^{16}\) Copyright 2017. The contact angle of a water drop on the surface when measured in sessile mode is $\theta = 91 \pm 1^\circ$.](http://pubs.acs.org/journal/acsodf)

![Figure 2. An 8 $\mu$L water drop ($B_o = 0.21$) evaporating on inclined substrates.\(^{16}\) Copyright 2017. (a) Change in the mass at different substrate inclination angles $\phi$. (b) Lifetime of the drop $t_F$ (i.e., the time required for the drop mass to reduce from $m$ at $t = 0$ to 0 at $t = t_F$) varies nonmonotonically, with $t_F$ being highest when the drop is inclined at $\phi = \pi/2$.](http://pubs.acs.org/journal/acsodf)
in altered depinning dynamics on the upper and lower sides of the drop as described below. The depinning force that acts at the upper (or lower) contact line is proportional to \(\sigma (\cos \theta (t) - \cos \theta)\) where \(\theta (t)\) is the instantaneous contact angle at the upper (or lower) contact line. In other words, due to a faster change in \(\theta\), the depinning force is larger at the upper contact line and thus the upper contact line recedes faster than the lower contact line. This gravity-aided faster depinning dynamics on parts of the contact line changes both the surface area available for evaporation \(S_{\text{deformed}}\) and the evaporative flux \(J\) at the interface, thus affecting the drying process.

Hence, it is clear that compared to a sessile drop, the depinning process is faster on the upper side of a drop residing on an inclined surface. If this depinning dynamics results in a substantial reduction in the area available for evaporation \(S_{\text{deformed}}\), then the drop on the inclined surface takes much longer to evaporate. This is cited as the reason for the increased lifetime of drops on orientated substrates in the experiments of Kim et al.\(^{16}\) (Figure 2). Of course, the particles if present in the drying drop can further delay this depinning dynamics and can influence the pattern formation as discussed in section 5.

It is well known that capillary flows are generated inside a pinned evaporating drop, which is one of the dominant mechanisms responsible for particle transport in drying drops. The analytical expression describing the capillary flows generated in undeformed drops drying on solid surfaces are available.\(^{2}\) However, such calculations for deformed drops are not generally possible. Instead, a semianalytical approach is followed in the literature.\(^{20,22}\) Assuming that the drops are two-dimensional, the velocity of the fluid averaged across the height of the drop due to capillary flow can be obtained as:

\[
u(x, t) = \frac{1}{h} \int \left[ J \left( \frac{\rho}{\rho} + \left( \frac{\partial h}{\partial x} \right)^2 + \frac{\partial h}{\partial t} \right) \right] dx
\]

where \(J\) is the evaporative flux at height \(h\) above the substrate at any location \(x\). In general, \(h\) is coupled to the stress field arising from the capillary flow, but in the case of slow evaporation, \(h\) may be determined from the hydrostatic pressure balance (eq 1). The only other parameter required to perform the integration of eq 3 is the evaporative flux \(J\) which can be calculated by solving the diffusion equation in the vapor phase.

5. Patterns from Particle-Laden Drops Dried on Inclined Surfaces

In this section, we will first analyze the patterns observed in various experiments of drying drops residing on substrates oriented at an angle with respect to gravity and then discuss the possible reasons leading to varied deposition patterns.

A straightforward route to understanding the role of gravity in pattern formation is to compare the patterns obtained by drops dried in sessile and pendant configurations. Figure 3 shows such a comparison of the patterns formed in three different experiments. In addition, this figure also illustrates the role of particle concentration, the size of the dispersed particles, and the substrate wettability on the deposit formation. It may be observed that, independent of the configuration of the drop, a coffee ring is obtained when dilute dispersions of smaller particles are dried on hydrophilic substrates. However, a change in any of these parameters may make the deposits of sessile and pendant drops nonidentical. Figure 3a by Sandu and Fleaca\(^{22}\) illustrates that as the concentration of particles is increased, a pendant drop generates a strong coffee-eye-like deposit as opposed to the weak central deposit found in sessile drops. As shown in Figure 3b reported by Li et al.,\(^{23}\) larger particles alter the spatial distribution of particles in dried sessile drops, and for the largest particles studied, it is observed that the patterns are irregular with a significant concentration of particles in the central region as well. In the corresponding patterns obtained by evaporating pendant drops containing larger particles, coffee rings completely disappear, and a thick deposit which spans an area much smaller than that observed in sessile drop is generated. Figure 3c as reported by Mondal et al.\(^{7}\) shows that a strong coffee eye is produced in pendant drops on neutrally wetting \((\theta = 90^\circ)\) substrates. These experiments illustrated that a decrease in substrate wettability reduces the strength of the coffee eye while no central deposition is observed in corresponding deposits from sessile drops. But, of course, a
reduction in wettability generated weaker coffee rings from drying sessile drops.

The picture that emerges from the above discussion regarding Figure 3(a–c) is that dried particle-laden sessile drops always produce coffee rings when dilute dispersions of smaller particles are dried on a hydrophilic substrate. In contrast, drying pendant drops always generate patterns where the concentration of particles at the center is higher compared to that on the edge. The difference in the concentration of particles at the edge and the center depends on the initial concentration of particles in the dispersion, the size of the particles, and the wettability of the substrate. While the accumulation of particles in the patterns resulting from the dried pendant drops shown in Figure 3b,c is driven by the gravity settling of the particles and particle aggregates, the patterns in (c) demonstrate that the central deposition is dictated by the effect of gravity on the drop shape, an aspect that is discussed further in this section.

A comparison of deposits obtained from drops dried on inclined surfaces is shown in Figure 4. Experiments' using hematite particle dispersions dried on vertical substrates show stronger deposits on the lower contact line, but the extent of distribution is found to be a function of the substrate wettability and hence the drop shape. The less wettable the surface, the greater the concentration of particles deposited at the lower contact line. Similarly, dispersions of spherical polystyrene particles dried on a neutrally wetting (θ = 90°) vertical substrate (φ = 90°), adapted with permission from Mondal et al.7 Copyright (2018) American Chemical Society. (b) Drop (1 μL) containing 1 wt % of 3 μm diameter polystyrene particles dried on a neutrally wetting (θ = 90°) vertical substrate (φ = 90°), adapted with permission from Mondal et al.7 Copyright (2018) American Chemical Society. (c) Strip of coffee, Bo = 0.5, dried on a hydrophilic substrate inclined at an angle of φ = 10°, Du and Deegan,20 reproduced with permission. (d) Drop of an aqueous solution of ferroin dried on a vertical substrate, Du and Deegan,20 reproduced with permission. The direction of gravity is from top to bottom in all cases.

Figure 4. Comparison of deposit patterns obtained from the drying drops of colloidal dispersions on substrates inclined at an angle φ: (a) 2 μL drops containing hematite ellipsoids (∼59 nm diameter, ∼244 nm long) at a concentration of 0.12 wt % dried on a vertical substrate of various wettabilities, adapted with permission from Mondal et al. Figure 4 shows the patterns obtained from drying a drop residing on a vertical substrate compared to that of a drop dried in both sessile and pendant configurations.24 Irrespective of the orientation of the substrate, the patterns appear as a coffee ring when observed under an optical microscope (top view). However, as seen in the set of images at the bottom, the height profiles measured by a surface profilometer give a quantitative difference in the coffee rings. The width of the coffee ring appears to be slightly larger in a pendant drop. For the drop that resided on the vertical substrate, the height of the deposit varies in the azimuthal direction with the ring being widest and highest at the lower contact line. This increased height at the lower contact line is almost double compared to the height of the deposit patterns obtained from dried sessile and pendant drops. Therefore, microscopy images alone do not capture the effect of gravity, and alternative characterization techniques must be used in tandem.

While central deposits in pendant drops and one-sided deposits in drops dried on inclined surfaces seem to be common features as seen in Figures 3 and 4, the way gravity effects come into play in each case is different. Gravity can affect the pattern formation in drying drops in two different ways: gravitational settling of the particles referred to here as a direct effect and the gravitational deformation of the drop which affects the evaporation kinetics and the particle transport mechanisms, referred to here as the indirect effect.

5.1. Direct Effect. A convenient way to assess the importance of gravity compared to thermal fluctuation in drop drying problems is in terms of the Peclet number defined as the ratio of gravitational force to Brownian force

\[ P_e = \frac{\pi d_p^4 \rho \Delta \rho}{12 k_B T} \]  

where \( d_p \) is the particle diameter, \( \Delta \rho \) is the density difference between the particle and the liquid (or suspending medium),
and \( k_B \) is the Boltzmann constant. If the particles are sufficiently denser than the carrier liquid and thermal forces are weaker compared to gravity, then \( Pe_g > 1 \). In such scenarios, the particles in the drying drops undergo gravitational settling.\(^{23} \) Since the particle Reynolds number is much less than 1, the settling velocity of a single spherical particle can be calculated using Stokes’ law:\(^{17} \)

\[
u_p = \frac{g \rho_p^2 \Delta \rho}{18 \mu} \tag{5}\]

The nonspherical shape of the particles, electrokinetic effects that may arise from the charges on the particle, and hydrodynamic interactions between the particles can alter the velocity calculated from eq 5. Whether the gravitational settling influences the spatial distribution of particles in the evaporative deposits also depends on the height of the drop (\( h \)) and the total drying time (\( t_d \)). We can define a nondimensional parameter, \( \frac{u_p t_d}{h} \), the ratio of length that the individual particles in the drop traverse during the course of drying to the height of the drop. If this ratio is greater than 1, then the particles are expected to settle on the substrate on which the sessile drops are dried. It is also possible that the particles in the drying drop can aggregate and settle on the substrate during the evaporation process.\(^{22,23−28} \) It may be noted that settled particles or aggregates can also be transported towards the contact line depending on the strength of the evaporation-driven radial flow, yielding a typical coffee ring pattern. While the particles settle on the substrate in drying sessile drops, the particles settle toward the apex of the drop in drying pendant drops. The accumulation of particles in the apex region, if it remains undisturbed until the end of the drying period, will result in a pattern with central deposit vis-à-vis a coffee-eye pattern.\(^{26} \) Such deposit patterns can be manipulated by carefully tuning the size of the particles, the concentration of the particles, and the drop volumes, thus obtaining thick self-assembled photonic crystals of nanoparticles.\(^{24,27} \) The evaporation of drops containing mixtures of particles of different sizes, when dried in sessile and pendant modes, can lead to contrasting patterns solely due to the effect of gravity on the particles.\(^{29} \) On inclined substrates, gravity-driven settling of the particle aids in the deposition of particles at the advancing end of the drop and hinders the deposition at the receding end.

### 5.2. Indirect Effect

In many drying drop experiments, the size of the dispersed particles is too small to experience the effect of gravity directly (i.e., \( Pe_g < 1 \) and \( \frac{u_p t_d}{h} < 1 \)). However, regardless of the size of the dispersed particles, the carrier fluid drop may still deform under the action of gravity as described in section 3, which may also cause the deposition patterns to differ. The deformation is axisymmetric for a sessile and pendant drop, but the deformation is nonaxisymmetric for drops residing on an inclined plane and typically their lower (front) contact angle is larger than the upper (rear) contact angle. This gravity-induced drop deformation, whether axisymmetric or not, can affect the particle transport mechanisms in the drying drop indirectly.

The classical mechanism suggests that the advective particle transport by the radially outward flow of carrier fluid is strongly dependent on the instantaneous contact angle of the drop on the substrate. For a sessile or a pendant drop, gravity-induced axisymmetric deformation will increase the interface area (\( S_{\text{deformed}} \)) available for evaporation, thus favoring faster evaporation. On the other hand, the axisymmetric deformation does not change the contact angle, and hence the nature of variation of evaporative flux near the contact line remains similar to the case of an undeformed drop. Therefore, compared to that of a spherical cap drop (\( Bo \ll 1 \)) there may be only a quantitative difference in the evaporation-driven flow set up inside an axisymmetrically deformed drop (sessile or pendant) and the particles being carried and deposited by this flow field.

In contrast, gravity-deformed drops residing on an inclined surface are nonaxisymmetric; therefore, the evaporation flux and the advection of particles toward the contact line are also nonaxisymmetric. However, this nonaxisymmetry does not
directly explain the various patterns discussed in Figures 4 and 5. Simulations in two dimensions reported by Du and Deegan show that the deposit on the upper side will grow faster than that on the lower side since the upper (rear) contact angle is smaller than the lower (front) contact angle. However, gravity also aids in the depinning of the upper contact line. Hence, it is found from the calculations that the drying of smaller droplets which do not depin easily results in deposits with a higher particle concentration at the upper edge of the drop, but in the case of larger drops which depinned easily, the deposits formed will have a higher concentration of particles on the lower side of the contact line. Since the theoretical developments concerning the evaporation-driven flows in drops on inclined surfaces are sparse, further studies are warranted to unearth the physics of pattern formation.

On the other hand, the patterns may differ if the particle transport is mediated by the interface, an aspect which has been far less explored compared to the advective transport of particles through the bulk in studies involving evaporating drops. As drying proceeds, dispersed particles may get adsorbed at the interface. This may be because of the weakly charged nature of the dispersed particle or simply because the interface sweeps the particles as drying proceeds even if the particles are highly charged. Once the particles are adsorbed, high detachment energy keeps them at the interface. An adsorbed particle migrates on an interface to regions of higher curvature in order to reduce the interfacial energy of the system. The strength of this migration depends upon the mean and deviatoric curvatures (average of and difference in principal curvatures, respectively) of the interface. In a sessile drop, both the mean and deviatoric curvatures increase from the apex of the drop toward the contact line. In a pendant drop, the mean curvature is maximized at the apex of the drop, while the deviatoric curvature is maximized at the contact line. For a drop residing on an inclined plane, both the mean and deviatoric curvatures change at every location on the surface such that the hydrostatic force balance between gravity and the surface tension force is maintained. Therefore, depending upon the direction in which the curvatures of the interface change, curvature-driven particle migration along the interface may give rise to different patterns than that predicted by the advective particle transport route driven by evaporative flux.

Another scenario arises if the concentration of particles is relatively lower and the interface is shrinking very fast. Then it is likely that all of the particles may get adsorbed to the interface before the convective currents or gravity can deposit them. In such a case, instead of coffee-ring formation, a uniform deposit of particles is formed. Such uniform deposits can also form if the particles in the drying dispersion drop preferentially adsorb to the interface. If such processes are dominant, even a drop residing on an inclined surface can give rise to uniform deposits, though the deposit itself may not be circularly symmetric. However, this has not been explored to date.

Thus, it is easier to understand the direct effect of gravity on the distribution of particles in the deposit patterns generated; the indirect effect arising though the drop deformation is complex due to the interplay between the shape and the various competing particle transport mechanisms.

6. SUMMARY AND PERSPECTIVES

Drying drops of colloidal dispersions residing on a solid substrate is exceedingly rich in physics on various scales: (i) The width of the contact line, the smallest length scale, that dictates the pinning or depinning movement of the contact line is crucial in determining the rate of the evaporation process and hence the deposit patterns obtained. (ii) The next longest length scale that is relevant is the length scale over which dispersed particles interact via short-ranged electrostatic and other interaction forces. These forces determine the colloidal stability of particles inside the drop and the spatial organization of particles such as ordered and disordered regions in deposit patterns. (iii) The third longest length scale in the problem is the size of the particles themselves. This is the length scale over which the direct effect of gravity discussed in section 5 and the hydrodynamic interactions come into play. (iv) The next in order is the size of the drop itself. At this length scale, gravity and surface tension forces act to determine the shape of the drop. Bulk processes such as evaporation-induced flows, the advection of particles, and vapor diffusive transport into and out of the drop will occur at this length scale. This length scale influenced by gravity effects leads to the indirect effects that dictate the patterns formed from the drying of deformed drops as discussed in section 5. While the processes on the first two length scales are unaffected by gravity, the processes that occur on the particle and drop length scales may or may not be affected by gravity depending upon the size of the dispersed particles and the drop.

The drying of drops of colloidal dispersions is an example in which the simultaneous and coupled transport of mass, momentum, and heat occurs. This includes the evaporation of liquid into the surrounding air, thermal Marangoni stress-induced fluid flows, the advective transport of particles, flows set-up due to external additives, heat transport due to temperature gradients set up in the system as a result of evaporation, and heating of the substrate or the surroundings. Because gravity plays a major role in determining the shape of the drop and the fact that the transport processes discussed above are indeed dependent on the geometry of the drop, the kinetics of drop evaporation and the distribution of particles in the final deposit patterns are bound to be different from the patterns obtained when undeformed drops are dried. This review calls for directed efforts to delineate the role of different processes that dictate patterns from drops dried in a nonsessile configuration. For example, the bulk flows set up by Marangoni stresses are shown to significantly alter the patterns from a dried sessile drop. Because surface tension is a function of temperature (surface tension − temperature coefficient for water is $\beta = -0.15$ mN/m K), temperature differences induce Marangoni flows. Therefore, when the substrate or the ambient environment is heated, Marangoni flows that act against the radial capillary flow become important and can suppress coffee ring formation. This has been studied experimentally and numerically. However, the temperature profiles and their effect on particle transport in drops on inclined surfaces have not yet been investigated.

From the highlights presented in this mini-review, it is clear that there are fewer theoretical and computational studies of the drying of deformed drops containing colloids compared to the number of experimental investigations. Any theoretical framework needs to take into account all three transport processes discussed above, thus making the analytical progress cumbersome. The presence of multiple length scales and an evolving geometry due to evaporation escalate the difficulties. The attempt to investigate these effects via numerical simulations is equally hard. Of course, the above picture becomes more intricate to account for other effects such as particle anisotropy and surface charges, solutal Marangoni flow due to the presence...
of surface-active species, and soft and patterned solid substrates to name a few.

Recent studies have shown the importance of the role of gravity in evaporating binary fluid drops. Similar to the thermal Marangoni effect, in binary fluid drops, the difference in volatility leads to differential evaporation of the components setting up Marangoni-driven internal flows. These are shown to depend on the orientation of the substrate on which the drops reside. However, the role of these flow fields in the deposition of particles in drops residing on inclined surfaces is yet to be understood.

This mini-review brings out the fact that the role of gravity may not always be negligible and should be taken into account in the analysis of the drying of drops in general and drops residing on inclined surfaces in particular. Therefore, it would be interesting to exploit the directionality induced by gravity in the evaporative patterning of colloids on solid surfaces. For example, carefully designed drying drop experiments show that the patterns obtained from dried sessile and pendant drops are distinctly different yet azimuthally symmetric. This azimuthal symmetry is absent in the patterns from the drops dried in any other orientation. Hence, it may be desirable to analyze the symmetry broken by gravity in order to identify the role of various mechanisms during drop drying. As discussed in this mini-review, such investigations will help to unravel the mechanisms at play as well as bring in new effects that will benefit the aspiring field of self-assembly. Both direct and indirect effects of gravity on drying drops may have implications in medical and forensic investigations where dried blood patterns assume importance.

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**Notes**

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