Evaporation of a Sessile Colloidal Water–Glycerol Droplet: Marangoni Ring Formation

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ABSTRACT: The transport and aggregation of particles in suspensions is an important process in many physicochemical and industrial processes. In this work, we study the transport of particles in an evaporating binary droplet. Surprisingly, the accumulation of particles occurs not only at the contact line (due to the coffee-stain effect) or at the solid substrate (due to sedimentation) but also at a particular radial position near the liquid–air interface, forming a “ring”, which we term as the Marangoni ring. The formation of this ring is primarily attributed to the solutal Marangoni flow triggered by the evaporation dynamics of the water–glycerol droplet. Experiments and simulations show fair agreement in the volume evolution and the general structure of the solutal Marangoni flow, that is, the Marangoni vortex. Experiments show that the location of the Marangoni ring is strongly correlated with the Marangoni vortex. However, finite element numerical simulations fail to describe the particle distribution seen in the experiments. Interestingly, the particles not only accumulate to form the Marangoni ring but also assemble as colloidal crystals close to the liquid–air interface, yielding iridescence. The formation of the colloidal crystals in the experiments is strong evidence that non-hydrodynamic interactions, which are not represented in the simulations, also play a significant role in our system.

INTRODUCTION

Multicomponent sessile droplets containing colloidal particles are ubiquitous in nature and technology. Even though a colloidal droplet seem to be a simple system, evaporation leads to a complex physicochemical scenario involving evaporation-driven flows, segregation, phase-separation, and flow patterns driven by gradients in concentration and temperature, and density. The fluid flow inside the droplet strongly determines the transport of the dispersed particles. Understanding the transport of particles is important in scenarios such as biofluid droplets, electronics, inkjet printing, and catalysis.

The radially oriented capillary flow in a pinned evaporating droplet can transport particles toward the contact line, forming the so-called coffee-stain deposits. However capillary flow is not the only evaporation-driven flow that can appear in a droplet. Preferential evaporation at the contact line of a multicomponent droplet can also lead to a gradient in the interfacial composition along the liquid–air interface, generating interfacial Marangoni shear in, for example, salt mixtures or surfactant solutions. Thermal gradients can also easily appear, leading to interfacial thermal Marangoni shear stresses. These gradients in composition and/or temperature, lead to gradients in surface tension, producing solutal and/or thermal Marangoni flow. These interfacial flows add up to complex flow patterns within the evaporating droplets. Occasionally, such flow patterns might prevent the particles to reach the contact line, suppressing the formation of the coffee ring. In other instances, such flows might provide an alternate route for the particles to reach the contact line.

However, Marangoni flow can also cause the accumulation of particles at the liquid–air interface. For example, thermal Marangoni flows are known to drag particles away from the contact line toward the droplet’s apex. Particles accumulate in the central region of the interface, forming a cap with a dense border, which we will term from now on as “Marangoni ring”. Such a cap with visible rings was already described by Deegan et al. and more recently studied by Parsa et al. and Zhong and Duan, when particle-laden droplets were evaporating on substrates at high temperatures. Rossi et al. also found an inner ring in water droplets having small amounts of mineral salts. Particle-laden droplets evaporating at very low pressures also show an inner ring. In all these cases, the thermal Marangoni flow transports the particles along the liquid–air interface away from the contact line and toward the inner ring. Similarly, when the droplet contains surfactants or surfactant-like polymers, the solutal Marangoni flow transports the particles along the liquid air interface and toward the inner ring.

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In this study, we will focus on the emergence of Marangoni rings in droplets containing a mixture of two liquids. In such a binary droplet, the properties of the individual liquids, such as their volatility, mass density, surface tension, and viscosity, determine the nature of the fluid flow. Mixtures of water and glycerol are of special interest, for instance in inkjet printing, laboratory studies, and biological processes. The high viscosity, miscibility in water, low cost, and non-toxic nature makes glycerol an excellent thickener for consumer products.

In this work, we show that a particle-laden binary droplet of water and glycerol shows a very distinct Marangoni ring similar to droplets containing only one liquid. To the best of our knowledge, this is the first detailed study of the spatio-temporal evolution of the Marangoni ring in a binary droplet. We use high-resolution confocal microscopy and explore a wide range of initial glycerol concentrations and different particle types. Three-dimensional velocity measurements and finite element simulations are performed to understand the formation of the Marangoni ring in this system. Our experiments show colloidal crystallization and iridescence close to the Marangoni ring, a strong indication of the relevance of non-hydrodynamic interactions between the different particles and between the particles and the liquid—air interface.

## EXPERIMENTS AND METHODS

### Chemicals and Materials

The following chemicals were used as received: acetone [Boom BV, ≥99.5% (v/v), technical grade], ethanol [Boom BV 100% (v/v), technical grade], and glycerol (Sigma-Aldrich, ≥99.5%, ACS reagent). Non-fluorescent silica particles (diameter = 0.970 μm, SD = 0.029 μm, aqueous suspension), non-fluorescent polystyrene (PS) particles (diameter = 1.05 ± 0.04 μm, aqueous suspension), and fluorescent PS particles (PS-FluoRed-particles, diameter = 0.980 μm, SD = 0.04 μm, abs/em = 530/607 nm) were obtained from Microparticles GmbH, Germany. Fluorescent rhodamine B-labeled silica particles. The confocal microscope was operated in the resonant mode with a Plan Fluor 10X DIC objective and having an in-plane resolution of 2.5 μm/pixel. The three-dimensional particle distribution is reconstructed by combining images from horizontal planes which are separated by approximately 5 μm distance. It takes approximately 1 s to collect the signals from all the horizontal planes for each time step, which is sufficiently fast as compared to the evaporation time of hundreds of seconds. The confocal microscope was also operated separately in the Galvano mode at low magnification (with a Plan Fluor 4X objective having in-plane resolution of 6.2 μm/pixel) at 5 s per frame to obtain particle distribution in the entire droplet within the field of view.

### Measuring the Spatio-Temporal Particle-Distribution in the Droplet

A laser scanning fluorescence confocal microscope (Nikon confocal microscopes A1 plus system) was used to obtain the spatio-temporal distribution of the particles inside the evaporating droplet (Figure S1b). A laser with a wavelength of 561 nm, filter cube (590/50 nm), and DU4 detector were used to observe the fluorescent rhodamine B-labeled silica particles. The confocal microscope was operated in the resonant mode with a Plan Fluor 10X DIC objective and having an in-plane resolution of 2.5 μm/pixel. The three-dimensional particle distribution is reconstructed by combining images from horizontal planes which are separated by approximately 5 μm distance. It takes approximately 1 s to collect the signals from all the horizontal planes for each time step, which is sufficiently fast as compared to the evaporation time of hundreds of seconds. The confocal microscope was also operated separately in the Galvano mode at low magnification (with a Plan Fluor 4X objective having in-plane resolution of 6.2 μm/pixel) at 5 s per frame to obtain particle distribution in the entire droplet within the field of view.

### Measuring the Flow-Field in the Droplet

To determine the evaporation-induced flow in the droplet, we performed micro particle image velocimetry (μPIV) and three dimensional particle tracking velocimetry (3D-PTV).

μPIV. 2D velocity fields are measured by μPIV using fluorescently labeled silica particles dispersed in the droplet and observed using the confocal microscope in resonant mode with a Nikon 20X water immersion objective of numerical aperture 0.5, yielding a resolution of 1.24 μm/pixel at 15 and 30 frame/s. The velocity field was obtained in a squared region of 0.636 mm × 0.636 mm (512 pixel × 512 pixel) close to the contact line in a horizontal plane approximately 10 μm above the solid substrate. The depth of correlation is estimated by the spread of the fluorescent microparticle’s image along the optical axis, which extends up to 10 μm approximately. Cross-correlations and the velocity field were obtained using PIVLab 2.53 (running in MATLAB) (see more details in Supporting Information, Section S3). The velocity field was averaged temporally over 0.33 s to obtain the final velocity distribution. To determine the average radial velocity as a function of the distance from the contact line, a rectangular strip of approximately 0.2 mm (along the contact line) × 0.6 mm (normal to the contact line) was selected, and the velocities were binned based on the distance from the contact line, with a bin size of 0.04 mm. Finally, the mean and standard deviation of the radial velocity is plotted.

3D-PTV. The three dimensional structure of the velocity field inside the droplet was measured by using general defocusing particle tracking velocimetry (GDPTV). To perform GDPTV, 1 μm diameter fluorescent PS particles were dispersed in a mixture of water and glycerol (particle concentration of approximately 5 × 10⁻⁵ w/v%). The motion of these particles inside an evaporating water—glycerol droplet was observed using an ECLIPSE Ti2 inverted microscope (Figure S1c). In GDPTV, the positions of the particles in the optical axis are obtained based on the characteristic particle image shapes at different distances from the focal plane. The main idea of the GDPTV algorithm is to rely on a reference set of experimental particle images at known depth positions which is used to predict the depth position of measured particle images of similar shape. The recorded microparticle images are processed using DefocusTracker 2.0.0 (running in MATLAB).
Finite Element Method Simulations of Evaporating Droplets. Numerical simulations are performed using an axisymmetric finite element method (FEM) approach to further understand the evaporating particle-laden water–glycerol droplet. The assumption of axisymmetry is justified for evaporating water–glycerol droplets as there are no instabilities that break the axisymmetry. On the contrary, such axisymmetry-breaking instabilities occur in evaporation of water–ethanol droplets or condensation of water-vapor on a pure glycerol droplet. To model the evaporation and the evaporation-induced flow within the droplet, the governing differential equations of continuity, mass transport, and momentum transport (Navier–Stokes) are solved for the water–glycerol mixture inside the droplet as well as for the water-vapor in the air surrounding the droplet.

In the gas phase, only diffusive transport of water vapor is solved, that is, Stefan flow and natural convection are disregarded. By using Raoult’s law generalized by activity coefficients predicted by AIOMFAC, the saturated vapor at the liquid–gas interface as function of the liquid composition can be imposed, whereas the ambient vapor concentration is imposed with a Robin boundary condition at the far field, mimicking an infinite domain. Glycerol is assumed to be non-volatile due to its low vapor pressure.

The diffusive flux of water vapor at the interface is used to account for the volume loss and the local composition change in the droplet domain. The contact line is assumed to be pinned, where a tiny slip length (1 μm) at the substrate is used to resolve the incompatibility of a no-slip boundary condition at the substrate and the kinematic boundary condition with evaporation at the liquid–gas interface. In the droplet, the properties of the mixture, that is, mass density, dynamic viscosity, and diffusivity, are known functions of the local fluid composition, which have been obtained by fitting experimental data. The same applies for the surface tension at the liquid–gas interface, giving rise to a solutal Marangoni flow.

To monitor the distribution of particles, an advection–diffusion equation for a passive dilute continuous particle field is considered. The diffusivity of the particles is estimated using the Stokes–Einstein relationship.
equation and at the liquid−gas interface, the local increase of the particle concentration due to water evaporation is implemented. Of course, this approach does not allow for accurate particle−particle or particle−fluid interactions and hence loses its validity once the particle concentration exceeds the dilute limit. As long as the particles are dilute, however, reasonable results can be expected.

Finally, to accurately track the interface motion, the FEM uses an arbitrary Lagrangian−Eulerian (ALE) approach, where the mesh nodes are co-moved with the interface motion. The strongly coupled set of equations is discretized in space by triangular Taylor−Hood elements with first-order spaces for the vapor field, liquid composition, and pressure and second-order basis functions for the velocity. The equations are solved monolithically with a fully implicit backward differentiation formula of second order for the dynamic time stepping. The numerical method has been successfully applied in a widespread range of evaporating multicomponent droplets. More details on the method can be found in these references. The implementation is based on the free finite element framework oomph-lib.

To assess potential influences on the flow in the gas phase (Stefan flow, natural convection) and thermal effects (evaporative cooling, thermal Marangoni flow), these mechanisms have also been considered in additional simulations. However, the consideration of these mechanisms did neither influence the flow inside the droplet nor the volume evolution in a relevant manner, so that these mechanisms have been disregarded for simplicity.

**RESULTS AND DISCUSSION**

Evaporation Dynamics of Particle-Laden Liquid Mixture Droplets. The evaporation dynamics in liquid mixture droplets are far from trivial. Theoretical models, such as the celebrated model by Popov, are available to accurately predict the evaporation rate of sessile droplets of pure liquids. However, to the extent of our knowledge, there is no simple and generic analytical model available for evaporating sessile droplets of mixtures. Therefore, to understand the formation of the Marangoni ring, we first study the evaporation dynamics of the droplet (Figure 1).

The presence of contact line dynamics during the evaporation introduces an additional level of complexity to the process. Fortunately, for each of the compositions explored, the different modes of contact line motion are highly reproducible. Figure 1a−c shows the contact line dynamics of a particle-laden water droplet and water−glycerol droplet (w_g,i = 0 and 5%).

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Figure 2. Marangoni ring in a particle-laden water−glycerol droplet. (a) Top-view images of a water−glycerol droplet containing 0.8 μm sized silica particles (initial glycerol weight fraction, w_g,i = 5%). During evaporation, particles accumulate as a ring, termed as Marangoni ring, in between the contact line and the center of the droplet. (b) High-resolution fluorescence confocal microscopy image confirming the Marangoni ring (w_g,i = 5%, t/t_s = 0.6). The color shows the height of the particles from the substrate. (c) Vertical cross-section of the 3-D image in (b). The color shows normalized fluorescent intensity, which is representative of the particle concentration at a given location. The expected location of the air−liquid interface and liquid−solid interface is marked as a black dashed line. Marangoni ring forms close to the air−liquid interface. (d,e) Top-view images of the Marangoni ring in particle-laden water−glycerol droplets containing (d) commercial 1 μm silica particles and (e) commercial 1 μm PS particles (t/t_s = 0.4 and w_g,i = 5%).
For a water–glycerol mixture, $c_{w,s}$ is not a constant, but depends on the composition, according to Raoult’s law\(^\text{61}\) and the non-ideal behavior of water–glycerol mixtures. Thus, 
\[
\psi(x_g) = 1 - Ax_g
\]
(2)
Furthermore, by neglecting quadratic terms of $x_g$, we get
\[
\psi_{w,s} - \psi_{w,\infty} = (1 - (1 + A)x_g)c_{w,s}^0 - c_{w,\infty}
\]
(3)
We choose $A$ such that $\psi_{w,s} - \psi_{w,\infty}$ becomes zero at the same value of $x_g$ as when using the exact value of $\psi$ without linearization (Figures 1d and S3, Supporting Information). Hence
\[
\frac{dM_w}{dt} = -\pi D_w R((1 - (1 + A)x_g)c_{w,s}^0 - c_{w,\infty})f(\theta)
\]
(4)
Because the contact angles are very low, we can take $f(\theta) = 4/\pi$.\(^\text{53}\) Furthermore, the contact-line does not stay in constant contact angle or constant contact radius mode throughout evaporation, but rather shows various contact angle modes. Hence, for the purpose of solving this differential equation analytically, we take $R$ to be a constant (equal to the initial radius). We also assume that the composition in the droplet is spatially uniform. Thus
\[
\frac{d\tilde{M}_w}{dt} = \frac{\alpha}{\beta + \gamma \tilde{M}_w} - 1
\]
(5)
\[
(1 - \tilde{M}_w) - \frac{\alpha}{\gamma} \ln \frac{\beta - \alpha + \gamma \tilde{M}_w}{\beta - \alpha + \gamma} = \tilde{t}
\]
(6)

Figure 3. Velocity field in the droplet. (a,b) Simulations and (c) 3D-PTV measurements ($w_g = 25\%$) showing the vortex-like three-dimensional velocity field in the droplet. (b) Zoomed-in region of (a) close to the contact-line. The flow is radially outward in the lower region of the droplet and radially inward in the vicinity of the air–liquid interface due to the presence of Marangoni shear. $R$ is the radius of the droplet and $r$ is the radial location from the center of the droplet; thus, $R - r$ shows the distance from the contact line. The velocities are low away from the contact line ($R - r > 0.5$ mm). For 3D-PTV, a very low concentration ($\approx 5 \times 10^{-8}\%$ w/v) of fluorescent PS particles was used (see Experiments and Methods). The velocity field in (c) is constructed by superimposing the particle-trajectories over 100 s. The green dash-dotted line in (c) shows the expected location of the air–liquid interface.

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where

\[
M_w = \frac{M_{w,i}}{M_{w,i}}
\]

(7)

\[
\beta = \frac{M_{g,i}}{M_{w,i}}
\]

(11)

\[
\gamma = \frac{\mu_g}{\mu_w}
\]

(12)

Here, \(M_{g,i}\) is the initial mass of glycerol in the droplet; \(M_{w,i}\) is the initial mass of water; \(\mu_g\) and \(\mu_w\) are the molar masses of glycerol and water, respectively; and \(c_{w,\infty} = c_{w,0} \times \text{RH}\), where RH is the relative humidity far from the droplet. We used the relative humidity as a fitting parameter between the experiments and the analytical model for particle-laden droplets of water \((w_{g,i} = 0)\), giving RH = 38% in the model (Figure 1c). This value of RH was used in the simulation and the analytical model for all other values of \(w_{g,i}\).

\[
\alpha = (1 + A) \frac{c_{w,s}}{c_{w,s} - c_{w,\infty}} \frac{M_{g,i}}{M_{w,i}}
\]

(10)

Figure 4. Radial velocities close to the substrate. Velocity in a horizontal plane close to the substrate in experiments and simulations, at various time instances, are plotted for a droplet with initial glycerol weight fractions, \(w_{g,i}\), of (a) 0.5, (b) 5, and (c) 25%. \(R - r\) is the distance from the contact line. In simulations, for the cases where the air–liquid interface close to the contact-line is deformed strongly by Marangoni contraction (see Supporting Information, Figure S8), \(R - r\) refers to the distance from the apparent contact line, instead of the imposed contact line. The experimental results are from \(\mu\)PIV measurements. The velocities plotted for each \(w_{g,i}\) are averages from three independent experiments, vertical error bar shows the standard deviation, and horizontal error bars represent the size of interrogation window used in performing \(\mu\)PIV. All the droplets contained 0.1 wt % of 800 nm fluorescent silica particles at the beginning of evaporation.
Figure 1e–i shows the excellent agreement between simulations, experiments, and the analytical model. During the initial part of the evaporation, $M_w$ decreases almost linearly with $\tilde{t} = t/t_s$ (Figure 1). For large times, $M_w$ approaches the asymptotic value of $M_w^* = \frac{e_{w,i} - e_{w,oo}}{\tilde{r}}$, when $e_{w,i} - e_{w,oo}$ becomes zero. The deviations between the simulation and the analytical model can be attributed to the assumption of a perfectly mixed droplet in the analytical approach. Overall, the good agreement of experiments and simulations with the theory shows that, in line with expectations, the evaporation can be modeled as a diffusion-limited process.

Formation of the Marangoni Ring. Figure 2 shows the formation of the Marangoni ring observed using different experimental methods (for $w_{g,i} = 5\%$). During the evaporation of a particle-laden water–glycerol droplet, a bright ring forms in between the contact line and the center of the droplet which we identify as the Marangoni ring (Figure 2a, Supporting Information, Video V1). This ring appears $17 \pm 6$ s after the drop is deposited on the substrate.

Confocal microscopy shows that this ring corresponds to a dense accumulation of silica particles (Figure 2b,c, Supporting Information, Video V2). We additionally confirmed that the Marangoni ring is not limited to a particular choice of particles and initial glycerol weight fractions. Both commercial PS particles and commercial silica particles of diameters 1 $\mu$m form similar Marangoni rings (Figure 2d,e, Supporting Information, Videos V3 and V4). For all these three cases (Figure 2a,d,e), the initial glycerol weight fraction ($w_{g,i}$) is 5%. A Marangoni ring also forms for silica particles of diameters 0.8 $\mu$m at other initial glycerol weight fractions, viz. $w_{g,i} = 0.5, 25,$ and $50\%$ (Figure S4).

Why do particles form the Marangoni ring in a binary droplet? To answer this question, we first look at the flow-field in the droplet.

Flow Field in the Droplet. Particle motion within an evaporating droplet is predominantly governed by the fluid flow. In our water–glycerol droplet, the values of the Rayleigh number $Ra = 2 \times 10^5$, the Marangoni number $Ma = 4 \times 10^5$, and the contact angle $\theta = 10^\circ$ clearly indicate a surface-tension-driven Marangoni flow, instead of a buoyancy-driven flow (cf. Figure 6a of Diddens et al. and Supporting Information, Section S7 here). This Marangoni flow arises because of differences in the volatility and surface tension of water and glycerol, with glycerol being non-volatile and with lower surface tension than water (63 vs 72 mN/m, respectively). Due to the depletion of water at the contact line, a surface tension gradient arises toward the droplet’s apex, which leads to a Marangoni shear in the same direction. Consequently, the interfacial flow is...
directed from the contact line toward the droplet apex, as seen in the experiments and simulations (see Figure 3).

The strong interfacial flow, combined with the capillary flow, \(^3\) generates a vortical flow structure which we will refer to as “Marangoni vortex”, typically present in evaporating droplets with strong interfacial flows, regardless of the origin of the Marangoni shear. \(^11,12,24,32,63\) However, simulations show that the Marangoni vortex spans along the whole droplet volume from the contact line to the droplet’s center (Figure 3a, Supporting Information, Video V5), while experiments show that the vortex is present mainly close to the contact line (Figure 3b and Supporting Information, Video V6)—in a similar way as observed in other droplets experiencing interfacial Marangoni flows. \(^11,24,32\)

Figure 4 shows a quantitative comparison of the velocity between experiments and simulations, in a plane approximately 10 \(\mu m\) above the substrate. As we move toward the center of the droplet in Figure 4, the outward radial velocity quickly peaks in the vicinity of the contact line and then decreases at a lower rate—achieving negligible values before reaching the droplet’s center. The simulations show a similar trend. However, they yield higher velocity values compared to experiments. Such a disagreement has been often found in water-based evaporating droplets where strong Marangoni flows are expected due to thermal\(^13,27\) or solutal gradients\(^12,64,65\) and can be explained by the presence of unavoidable interfacial contamination, which reduces the interfacial shear. The presence of interfacial contamination also explains the smaller Marangoni vortex in experiments compared to that observed in simulations. This is discussed in more detail along with additional simulations in Supporting Information (Section S10). Nonetheless, despite the quantitative differences, we can conclude that there is a fair overall qualitative agreement between flow-field observed in experiments and simulations (Figures 3 and 4).

In order to quantify the temporal changes in the velocity field during the evaporation process, we measure the size of the Marangoni vortex during a droplet lifetime (Figure 5a–c) by locating the point where the outward radial velocity drops below a threshold (chosen as 0.01 mm/s, see Figure 5e). The distance of this point from the contact line is denoted by \(L^*\). Figure 5 shows that the size of the Marangoni vortex initially increases with time and then decreases close to the end of evaporation.

**Marangoni Ring—Spatio-Temporal Behavior.** Interestingly, the position of the Marangoni ring \(L\) from the contact line correlates well in time with the size of the Marangoni vortex \(L^*\) (Figure 5g–i, see Figures S6 and S7 for additional data). Figure 5g–i shows that both \(L\) and \(L^*\) initially increase with time (growth phase), then reach a maximum, and finally decrease as time approaches the spreading time \(t_s\) (decay-phase). Thus, the location of the Marangoni ring correlates with the radial location where the particle velocity becomes very low. This correlation strongly suggests that the Marangoni ring formation may be governed by the flow-field in the droplet.

To get more information on the spatio-temporal distribution of the particles inside the droplet, we look at the three-dimensional particle distribution obtained from confocal microscopy of droplets containing the 0.8 \(\mu m\) fluorescent silica particles (Figure 6). The particle distribution is nearly uniform in the early moments of evaporation (Figure 6, \(t/t_s = 0.05\)) and eventually, as evaporation progresses, the particles accumulate at different locations along the liquid–air interface (Figure 6). The particle concentration peaks: (1) at the contact line (CL), (2) at

![Figure 6](https://doi.org/10.1021/acs.langmuir.2c01949)

**Figure 6.** Spatial distribution of particles. Normalized fluorescent intensity of 0.8 \(\mu m\) silica particles in a vertical cross-section of the droplet observed using fluorescence confocal microscopy for initial glycerol weight fractions \(w_{gi} = 0.5\) (a–c), 5 (d–f), and 25\% (g–i), at \(t/t_s = 0.05\) (first column), 0.3 (second column), and 0.6 (third column). Darker color indicates a higher particle concentration. The expected location of the air–liquid interface is marked as a black dashed line. However, we note that the precise location of the air–liquid interface cannot be determined with the shown data. The contact line (CL), Marangoni ring (MR), and cap region (CP) are marked in the images. Vertical scale bar: 0.05 mm and horizontal scale bar: 0.2 mm. All the droplets contained 0.1 wt % of 800 nm fluorescent silica particles at the beginning of evaporation.

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### Table 1

| \(w_{gi}\) | \(t/t_s\) | Clustering Location |
| --- | --- | --- |
| 0.5\% | 0.05 | CL, MR, CP |
| 5.0\% | 0.3 | MR, CP |
| 25\% | 0.6 | MR, CP |

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1. \(^3\) Data from previous studies.
2. \(^11\) Further details can be found in the Supporting Information.
3. \(^24\) Additional analysis is provided in Section S10.
4. \(^32\) Additional quantitative data is included in Figures S6 and S7.
Thus, the particles also accumulate to form the cap region between the Marangoni ring and the droplet apex (Figure 6), but usually with lower concentration compared to the Marangoni ring (see Figure 6i, Supporting Information, Videos V1, V3, and V4). Because the interfacial velocities are already very low in these regions, we suggest that the cap region is formed mainly because the particles are simply swept by the downward moving liquid–air interface.

A Peclet number of $Pe \approx 50$ in experiments supports the idea that the speed of the liquid–air interface is higher than the diffusion of the particles away from the interface ($Pe = \frac{v_{\text{interface}} h}{D}$, where $v_{\text{interface}}$ is the velocity of the interface, $h$ is the height of the droplet, and $D$ is the diffusion coefficient of the particles).

To verify whether there is a clear hydrodynamic mechanism behind the particle accumulation, we introduced the particle concentration in the FEM simulation as a continuous field advected by the evaporation-driven flow (see Experiments and Methods). Figure 7a,b compares the spatial distribution of particles inside the water–glycerol droplet, obtained in experiments and simulations. The experiments show a high particle concentration at approximately 0.5 mm from the contact line and 50 μm above the substrate (i.e., the position of the Marangoni ring, Figure 7a,c,e). However, while FEM simulations show that the particle concentration is high close to the air–liquid interface (Figure 7d), there is no local maxima of interfacial particle concentration between the contact line and the drop apex (compare Figure 7f with 7e). In fact, simulations predict that the particle concentration at the interface will be highest at the drop apex (Figure 7f). We conclude that the flow field obtained in the simulations cannot reproduce the Marangoni ring formation as seen in the experiments.

There are two main differences between the FEM simulations and the experiments, namely, (i) the crucial differences in the flow field and (ii) the lack of non-hydrodynamic particle interactions in the simulations. First, the Marangoni vortex in experiments is limited to a small region close to the contact line instead of spanning the whole droplet (Figure 3). Consequently, instead of being advected by the Marangoni vortex all the way to the droplet apex, the particles are concentrated in a smaller region, which is consistent with the experimental observations (Figure 7a,c,e).

Figure 7. Particle distribution in a droplet: experiments vs simulation. (a) Particle distribution inside a droplet visualized using fluorescence confocal microscopy. The colors show the normalized intensity of the fluorescence signal, as indicated by the color bar, and are representative of the concentration of particles. The black dashed line represents the estimated air–liquid interface. (b) Particle distribution inside a droplet as obtained using simulation. The colors show the normalized particle concentration. The horizontal lines in (a,b) show the location of the three planes located at $z = 10, 50$, and 100 μm. The particle distribution along these three lines are plotted against the distance from the contact line ($R - r$) in (c,d). The particle distribution close to the air–liquid interface is plotted for (e) experiments and (f) simulations. The simulations show that the particle concentration increases gradually as one moves from the contact line toward the apex of the droplet. In contrast, experiments show a distinct particle accumulation around 0.5 mm from the contact line, which corresponds to the Marangoni ring. The figure corresponds to a droplet with initial glycerol weight fraction $w_{\text{gi}} = 25\%$ at time $t/t_s = 0.3$. 

the Marangoni ring (MR), and (3) in the vicinity of the droplet’s apex, which we call the cap (CP).
the drop apex (as seen in simulations), the particles in the experiments are left at some point between the CL and the apex to form the Marangoni ring. The most likely reason for the mismatch between the velocity fields seen in the experiments and the simulations is the presence of contaminants in water-based systems, as often invoked and discussed.\textsuperscript{12,13,69,70} Impurities can easily neutralize the surface tension gradient, reducing the strength of the Marangoni flow with a small amount of contamination.\textsuperscript{65} Our additional simulations with insoluble surfactants further support this hypothesis (see Supporting Information Section S10 and Videos V5 and V7 for more details).

Second, the simulations only include hydrodynamic interactions. However, water–glycerol droplets containing 1 μm diameter silica and PS particles display a remarkable iridescence (Figure 8 and Supporting Information, Videos V3 and V4). The formation of such colloidal crystals is a signature of the closely packed arrangement of the colloidal particles. The photonic band gap created by the crystal structure causes the iridescence.\textsuperscript{71–73} Interestingly, for PS particles, the formation of these crystals coincides with the jumps in contact line of the droplet (Figure 8c,f; Supporting Information, Video V3). The formation of iridescent colloidal crystals in the experiments indicates that hydrodynamics is not sufficient to explain the phenomenon.

Future studies should look into controlling the surface properties of the particles to further understand the colloidal interactions responsible for the Marangoni ring formation. Including colloidal interactions along with hydrodynamics in simulations can also help us to further understand the process.\textsuperscript{31,60,74,75}

CONCLUSIONS

In this work, we discovered the formation of the Marangoni ring in an evaporating particle-laden water–glycerol droplet. The differences in volatility and surface tension of water and glycerol cause solutal Marangoni flow directed from the contact line toward the droplet apex. However, the interfacial flow loses strength before reaching the apex, and particles are left in an intermediate region, where their concentration increases. This is confirmed by the strong correlation shown between the thickness ($L^*$) of the Marangoni vortex and the position ($L$) of the Marangoni ring from the contact line. Simulations show that hydrodynamic interactions are not sufficient to explain why the local particle density increases to such an extent that colloidal crystals are formed near the liquid–air interface, as can be seen from the iridescence. It is not clear to us what the mechanism is that confines the colloidal particles in our system. Nonetheless, our results provide new insights into particle transport in colloidal droplets which might have important applications such as in diagnostics, inkjet printing, and production of functional coatings, novel opto-electronics, and pharmaceutical products.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.2c01949.

V1: Top-view imaging showing Marangoni ring formation in an evaporating water–glycerol droplet containing 0.8 μm silica particles (MP4)
V2: Fluorescence confocal microscopy showing Marangoni ring formation in an evaporating water–glycerol droplet containing 0.8 μm silica particles (MP4)

V3: Top-view imaging showing Marangoni ring formation and iridescence in an evaporating water–glycerol droplet containing commercial 1 μm PS particles (MP4)

V4: Top-view imaging showing Marangoni ring formation and iridescence in an evaporating water–glycerol droplet containing commercial 1 μm silica particles (MP4)

V5: FEM simulations of an evaporating water–glycerol droplet containing (passive) particles (MP4)

V6: Pathlines of particles tracked using GDPTV (MP4)

V7: FEM simulations of an evaporating water–glycerol droplet containing (passive) particles and insoluble surfactants (MP4)

Experimental setup; contact line motion; details of μPIV; linearization coefficient in evaporation model; Marangoni ring for various initial compositions; top-view visualization of particle-laden water droplet; calculations of Rayleigh and Marangoni numbers; additional data on contaminants (PDF)

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