Manipulating colloidal residue deposit from drying droplets: Air/liquid interface capture competes with coffee-ring effect

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HIGHLIGHTS

- Lagrangian particle tracking model of colloids within drying droplets.
- Relative roles of air/liquid vs. solid/liquid interfaces on the coffee ring effect.
- Critical line separates colloids captured first by free interface or by substrate.
- The descending air-liquid interface could capture a large portion of colloids.
- Regulating dried deposit by tuning the colloidal forces with air-liquid interface.

GRAPHICAL ABSTRACT
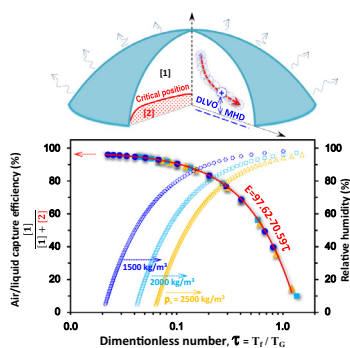
ABSTRACT

Significant efforts have been undertaken in recent years to understand, and ultimately control, the drying patterns of colloidal particle filled droplets on solid substrates. The ubiquitous coffee-ring effect has long been attributed to the drag of radial liquid flow towards the droplet edge, driven by diffusive evaporation. Here we report new results showing that there is a temporal competition between migrating colloidal particles, dispersed randomly inside a droplet, and the air/liquid interface in reaching the solid surface. Using the Lagrangian modelling approach to track the motion of colloidal particles within the evaporating droplets, we reveal a boundary line that separates colloidal particles into two groups: above it colloids are captured by the air/liquid interface prior to reaching the solid surface and vice versa. This critical line allows us to quantify the effectiveness of the two emerging routes for manipulating the coffee-ring effect, which work by controlling the interaction between colloids and either the substrate or the air-liquid interface. Our modelling results affirm recent experimental evidence that the air-liquid interface of sessile droplets plays a vital role in the formation of residual deposits. This improved fundamental understanding provides versatile strategies to control droplet deposition morphology, especially the most desired uniform deposit as well as an unusual "overhang" shape of the cross section of the ring-like deposits.

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1. Introduction

The ability to create uniform deposits of colloidal particles from drying droplets is highly desirable for many applications and has led to many attempts to eliminate coffee-ring type deposits. Generally, the self-assembly of colloidal particles inside an evaporating

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sessile droplet is strongly affected by the physical and chemical properties of particles, solvents and solid surfaces. Many important factors and parameters including capillary, thermal and concentration driven Marangoni flows (Hu and Larson, 2006; Nikolov et al., 2002), colloidal interactions among particles and between particles and surfaces, contact line motion, surface hydrophobicity and particle orientation have been examined and applied in controlling the particle deposit patterns. The focus has been on manipulating the convective fluid flows inside the sessile droplets. Accordingly, the assembly mechanism of the well-known coffee-ring deposits is assigned to the evaporation-driven radial capillary flow which drags colloidal particles from the bulk solution toward the three-phase contact line (TPCL) of the droplet edge (Deegan et al., 1997). On the other hand, the thermal Marangoni flow normally reverses the coffee-ring effect and ultimately forms a central bump of particles (Hu and Larson, 2006). However, these assembly mechanisms cannot explain many other particle deposit structures, especially, the uniform deposit patterns (Bigioni et al., 2006; Yunker et al., 2011) and the colloidal skin (Bigioni et al., 2006; Maki and Kumar, 2011) of particles formed along the air/liquid interface of the sessile droplets. Bhardwaj et al. (2010) proposed that a uniform deposit could be obtained if the transport of particles towards the solid substrate, controlled by attractive Derjaguin-Landau-Verwey-Overbeek (DLVO) forces dominates the particle motion to the edge by the radial outward flow and the Marangoni convection. This requirement is only satisfied under the condition of very slow evaporation rate or very small droplet and/or small contact angle since the DLVO forces are effective only within very short inter-surface distances (100 nm). However, the recent literature shows that a uniform deposit can be obtained for large drops (mm in diameter) evaporating under ambient (room) conditions. For instance, Yunker et al. (2011) found that ellipsoidal particles could form a uniform deposit rather than a coffee-ring deposit which was commonly obtained for the spherical particles. They proposed that the formation of a loosely packed structure of these ellipsoidal particles along the air/liquid interface could hinder the formation of the coffee-ring deposits. Similar results were reported earlier for a non-spherical sessile drops containing ligated gold nanoparticles (Bigioni et al., 2006). The transition from the coffee rings to uniform deposits was due to the jamming of particle monolayer on the air/liquid interface of the droplet. This uniform particle "skin" initially formed on the air/liquid interface could finally be deposited onto the solid substrate when the evaporating solvent was depleted, i.e., when the air-liquid interface disappeared on the solid-liquid interface. However, the physics of the particle accumulation along the air-liquid interface still remains poorly quantified.

Direct evidences of particle accumulation at the air/liquid interface of drying sessile droplets have been obtained by many advanced experimental techniques, including three-dimensional confocal microscopy (Yunker et al., 2011), optical coherence tomography (Trantum et al., 2013), optical microscopy (Bigioni et al., 2006) and fluorescence microscopy (Berteloot et al., 2012). However, the resolution limits of these optical techniques used to visualize the three-dimensional motions of liquids and particles inside sessile droplets have not allowed for accurate determination of the temporal and spatial changes in position of particles inside the droplets. This study aims to fill this gap of knowledge by applying the Lagrangian modelling approach to describe the particle motion inside a sessile droplet during the course of evaporation. The condition for particle deposition onto the solid/liquid and the air/liquid interfaces is established for different evaporation rates, initial droplet contact angles, particle densities, DLVO forces and microhydrodynamic resistance. By understanding transport and fate of colloidal particles within drying droplets, we then aim to compare the effectiveness of the two emerging routes for manipu-

lating the coffee-ring effect, which work by controlling the interaction between colloids and either the substrate or the air-liquid interface.

2. Mathematical modelling

The geometry used to develop a mathematical model for particle motion inside an evaporating sessile droplet is shown in Fig. 1. The droplet edge normally becomes pinned at the TPCL and evaporation cannot easily shrink the droplet base. In order to keep the droplet edge unchanged the liquid must flow towards the edge to refill the liquid lost at the edge by evaporation. If the sessile droplet contains suspended particles, they are dragged towards the solid surface by the liquid flow moving outwards to the droplet edge, leading the deposition of particles on the surface and at the edge known as the coffee-ring effect.

The sessile droplet is considered rotationally symmetric about the axis of symmetry of the spherical cap. A schematic representation of the expected trajectory of a particle inside a drying sessile droplet is depicted in Fig. 1. When the particle, dragged by the liquid flow, is close to the substrate, it will experience colloidal interaction forces and may deposit onto the surface if the attractive components are dominant (i.e. van der Waals force). However, if the particle is far away from the solid surface, the air-liquid interface descending towards to the solid surface may capture the particle before it can reach the surface. We can describe, therefore, an initial (virtual) boundary in the droplet; above this boundary we expect the particles to interact with the descending air-liquid interface before they can reach the solid substrate. It is our aim to quantify this boundary by applying the particle trajectory analysis and calculate the efficiency of particle deposition onto the solid surface as well as the efficiency of particle entrapment by the air/liquid interface. Here, the focus is on particle motion (non-Brownian) towards the solid substrate in competition with the descending air/liquid interface. The interactions between colloidal particles and the solid/liquid and air/liquid interfaces are based on the basic DLVO theory. More complex interactions with the air/liquid interface are not dealt with explicitly in this paper although we acknowledge their possible importance to a more complete understanding eventually.

2.1. Particle motion equation within an evaporating sessile droplet

We consider the migration of colloidal spheres under the influence of a liquid flow drag force, colloidal forces and gravitational forces. The effect of Brownian (thermal) diffusion (significant in quiescent fluids) on the particle motion is neglected as are the effects of inertial forces on the motion of colloidal particles.

The Stokes drag force on colloidal spheres is usually described by $6\pi\mu R_p(\vec{V} - \vec{W})$, where $\vec{V}$ and $\vec{W}$ represent the particle and liquid velocities, respectively, μ is the liquid viscosity and R_p is the particle radius. The commonly known Stokes drag is valid for particle motion far away from a solid surface. In the vicinity of a solid surface, however, the particle will experience an increased drag force due to the micro-hydrodynamic interactions caused by the drainage of an intervening liquid film. The Stokes drag force is then described by $6\pi\mu R_p(\boldsymbol{R_v} \cdot \vec{V} - \boldsymbol{R_w} \cdot \vec{W})$, where $\boldsymbol{R_v}$ and $\boldsymbol{R_w}$ are the tensors of microhydrodynamic (MHD) resistance of the particle motion and the fluid flow in the directions normal and parallel to the substrate surface, respectively (Nguyen and Schulze, 2004). The drag force is generally balanced by a number of non-inertial external forces including the gravitational force F_g, the van der Waals force F_{vdw} and the electrical double-layer (EDL) force F_{edl} (this assumption is valid when the time constant for the drag force