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Short Communication

# Agglomeration front dynamics: Drying in sessile nano-particle laden droplets

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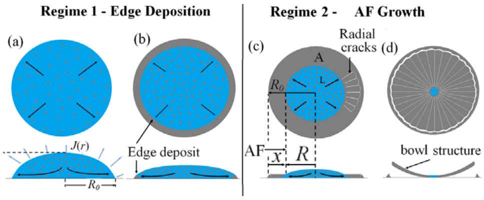
## HIGHLIGHTS

- Drying of nanoparticle laden droplets.
- Regimes of droplet drying identified based on deposit structure.
- The inward extension of the well known coffee-ring structure has been quantified.
- This inward growth has been found to be driven by droplet vaporisation and fast particle agglomeration.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The drying of sessile, nano-silica laden water droplet is studied under ambient conditions, in the absence of any convection. The drying process can be divided into two distinct regimes. During regime 1, the outer edge of the droplet remains pinned and particles agglomerate at the droplet periphery similar to the traditional coffee ring. However in regime 2, with further evaporation, both the liquid contact line and the agglomeration front starts moving radially inwards from the initial contact edge. The contact between the liquid and the agglomerate is maintained throughout regime 2 and the vaporisation driven liquid edge recession essentially drives the inward growth of the particle deposition. Fast kinetics of particle aggregation results in rapid growth of this agglomeration front as seen from the experiments. A theoretical formulation involving a simplistic model of the agglomeration front growth based on particle mass balance has been proposed.

## 1. Introduction

Controlled deposition of dissolved functional materials constitutes an important challenge in surface coating, inkjet printing and other emerging material deposition techniques. The deposition process is primarily evaporation driven coupled with particle transport in solution films. To understand the fundamentals of this deposition process, many previous works dealt with the evaporation of colloidal sessile droplets. Parisse and Allain (1996) used two models namely (i) constant base radius and (ii) constant droplet contact angle (previously developed by Picknett and Bexon (1977)) for pure liquid, to approximate the shape profiles during evaporation. They found that the first model gives a better approximation than the constant contact angle approach which is more suitable for pure liquid droplets. They argued that for correct shape calculation one needs to take into account an outward flow from droplet centre, induced by evaporation. Parisse and Allain (1997) further showed that evaporation which governs the droplet shape is influenced by the limited diffusion of solvent vapor in air. The outer flow of liquid induced by evaporation was investigated further by Deegan et al. (1997) by relating it to the evaporation flux. They predicted and showed experimentally that this outer flow causes the spherical particles in colloidal droplets to accumulate uniformly at the droplet edge to form the well known “coffee-ring” effect. The

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deposit growth at the droplet periphery was shown to follow a power law. Deegan et al. (2000) provided further quantitative analyses on the evaporation flux and the mass deposition, and argued that the coffee ring is universal for pinned contact line irrespective of droplet sizes and solvent type. Gravitational effects or external stimuli such as external heating or electric fields were argued to have no effect on the coffee ring pattern (Deegan et al., 2000).

Hu and Larson (2002), (2005) subsequently provided a more rigorous quantitative framework by deriving full solutions for the vaporisation flux and microscale flow velocity field inside the droplet for a wide range of contact angles (0–90°). For very thin droplets (low contact angle), Popov (2005) provided asymptotic solutions for the deposit parameters for the cases when the ratio of volume faction of solute in the liquid to that in the deposit approaches zero. Subsequent works have focused on nano-particle laden colloidal suspensions. They were shown to create strikingly different morphologies depending on the nature of the particles (Crivoi and Duan, 2013, 2013). Nano-silica laden aqueous sessile droplets drying on a substrate create an almost symmetric, flowery pattern with radial cracks and to some extent circular cracks (Jing and Ma, 2012). Significant works by Dufresne et al. (2003) explored the particle agglomeration in capillary tubes and subsequent cracking dynamics. They showed that when the colloidal suspension is allowed to dry from one end of the tubes, the transition from the liquid phase of the solution to densely packed compaction region is primarily a balance between the solvent vaporisation though porous agglomerate and the viscous flow resistance. Although their works did not involve sessile droplets, they provided considerable insight into particle agglomeration which can be readily extended to droplet drying. The deposit front growth in sessile droplets has been microscopically observed by Berteloot et al. (2012). They predicted the deposit growth to follow a power law i.e. $t^{2/3}$. However the work of Berteloot was mainly concerned with solutions with very low particle loading and large particle size (50 nm). Also their model was more towards quantifying the deposit growth in the initial stages of vaporisation. Bhardwaj et al. have studied the particle deposit shape in the cases of nano-particle laden nanolitre drops both experimentally and numerically. Their work has focussed on the effects of small scale interactions such as DLVO and Van der Waals forces on the nature of the final particle deposit (Bhardwaj et al., 2010).

Some works have even dealt with suppression of this apparent coffee ring feature altogether. For example, Hu and Larson (2005), (2006) showed that for organic fluids, latent heat of vaporisation drawn from the droplet can create non-uniform temperature field leading to dominant Marangoni flows. In such cases, recirculation is initiated in the two halves of the droplet that leads to particle deposition in the centre rather than the edge. For water droplets however, Marangoni effect was shown to be quite weak. They claimed that for water droplets, the inevitable presence of surface-active agents was probably why Marangoni effect was negligible. Thus the coffee-ring effect was common for droplets of aqueous solutions. Yunker et al. (2011) showed that the deposition pattern was dependent on particle shape. Using anisotropic particle shape (such as ellipsoidal), interparticle capillary interactions become dominant, and lead to an even distribution of particles after drying.

For nano-particle laden droplets, with evaporation of the liquid phase, particles agglomerate and form precipitate structure. Due to close packing of the particles in the precipitate, this structure starts from the periphery (coffee-ring) and with subsequent liquid evaporation and particle agglomeration, the precipitate structure proceeds radially inwards. Generally cracks are seen on the whole of the deposit structure (Parisse and Allain, 1997; Jing and Ma, 2012; Berteloot et al., 2012; Brutin, 2013; Goehring et al., 2013).

In the current work, based on experimental observation on drying sessile nano-particle laden droplets, we have formulated a theory governing the growth of the particle agglomeration front assuming fast kinetics of particle agglomeration. Beyond a certain nano-particle volume concentration, two distinct regimes have been demarcated: one being the edge deposition at constant liquid contact radius and the second being the inward extension/growth of the edge feature (agglomeration front—AF) along with the retreat of the liquid line. In the first regime, the particles agglomerate in the traditional coffee ring pattern while in the 2nd regime, the AF (the liquid—agglomerate contact line/interface) grows radially inwards as an extension of the coffee-ring structure. This inward growth of the AF is evaporation controlled and is mainly due to particle transport from liquid core (marked L in Figs. 1A and 2). The Reynolds number of the induced outward flow is low and also the

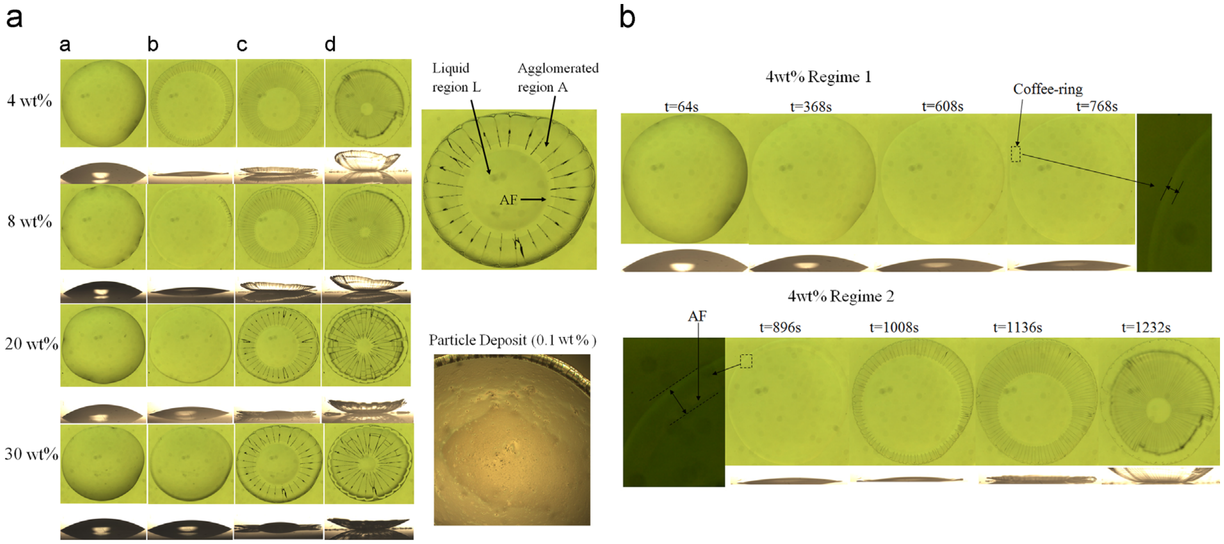

**Fig. 1.** (A). Images of droplet vaporization shown through top and side views, for different initial particle weight percentages. (a) The start of droplet vaporization with contact line pinned. (b) and (c) Advancement of the agglomeration front and inward radial crack propagation after completion of coffee-ring deposit. (d) Final structure. Top Inset—Close-up of phase (c) showing the liquid and the agglomerated regions along with the demarcation between the two i.e. the agglomeration front AF (agglomeration front) described subsequently. Bottom Inset—Close up of the final structure when starting particle concentration in droplet is taken as 0.1 wt%. Inner structure is markedly different from those for previous concentrations. (B) Images showing particle deposition as a continuous process from coffee-ring in regime 1 to AF in regime 2 for 4 wt%. Darkened close-up at the end of regime 1 and the beginning of regime 2 clearly shows the non-zero thickness of the coffee-ring as the initiation of AF growth occurs.