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# Influence of surface orientation on the organization of nanoparticles in drying nanofluid droplets

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ABSTRACT

The influence of droplet orientation on the flow directed organization of nanoparticles in evaporating nanofluid droplets is important for the efficiency of foliar applied fertilizers and contamination adhesion to the exterior of buildings. The so called "coffee ring" deposit resulting from the evaporation of a sessile nanofluid drop on a hydrophilic surface has received much attention in the literature. Deposits forming on hydrophobic surfaces in the pendant drop position (i.e. hanging drop), which are of importance in foliar fertilizer and exterior building contamination, have received much less attention. In this study, the deposit patterns resulting from the evaporation of water droplets containing silica nanoparticles on hydrophobic surfaces orientated in the sessile or pendant configuration are compared. In the case of a sessile drop the well known coffee ring pattern surrounding a thin nanoparticle layer was formed. A deposit consisting of a thin coffee ring surrounding a bump was formed in the pendant position. A mechanism involving flow induced aggregation at the droplet waist, settling, orientation dependant accumulation within the drop and pinning of the contact line is suggested to explain the findings. Differences in the contact area and adhesion of deposits with surface orientation will affect the efficiency and rainfastness of foliar fertilizers and the cleanliness of building exteriors.



## 1. Introduction

Increased crop yield by effective application of foliar applied fertilizer is necessary as the world's food requirements increase. Micronutrient containing nanofluids (i.e. fluid containing nanoparticles) are commonly sprayed as a fine mist onto the leaves of crops to combat nutrient deficiency and increase yield. Upon drying of the nanofluid drops, deposits of micronutrient nanoparticles on the leaf surface provide a source of micronutrients to the plant. The geometry of such a deposit will influence the uptake of nutrients (by nanoparticle to leaf contact area) and stability to environmental conditions (rain, wind, dew). Therefore, manipulating fluid and nanoparticle properties for effective deposit geometry is required to increase agricultural efficiency.

The deposit pattern resulting from an evaporating nanofluid drop has received a great deal of attention since the seminal article of Deegan et al. [1] on coffee ring deposit formation. Coffee ring deposits were explained to form due to the combined effects of particles pinning the contact line and differential evaporation rate over the droplet surface. As evaporation rate is greatest at the contact line, liquid from the bulk of the drop flows toward the contact line, carrying particles and forming a particle ring. Applications of such directed self assembly in an evaporating drop include inkjet printing [2,3], biosensors [4], DNA microarrays [5], and nanowires [6]. In comparison to these applications, much less research has been undertaken in the field of agrochemicals [7–10], especially foliar fertilizers.

A major difference between nanofluid foliar fertilizer and other applications is the orientation of the surface. The vast majority of research on the deposit pattern resulting from an evaporating nanofluid drop is performed using sessile droplets (i.e. drops on top of horizontal surfaces) on a hydrophilic surface. However, the surface of leaves can be hydrophobic and the position of the leaf is rarely horizontal. Also, foliar fertilizer drops are applied to both the upper and underside of leaves. A few examples of pendant drops (i.e. hanging drops) on a hydrophilic surface exist [11–13], but no examples of pendant drops on hydrophobic surfaces could be found from an extensive literature search. Contamination to the exterior of buildings and windows from pollution laden water droplets is another application in which surface orientation is important.

Is a fertilizer deposit pattern determined by leaf orientation and is pollution residue on the walls of buildings different to the eaves?

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It is the purpose of this article to provide further information to answer this question. Despite the initial expectation that surface orientation will not dramatically change the deposit pattern of small, slowly evaporating water droplets containing dilute and stabilized nanoparticles, we have found that droplet position (i.e. sessile and pendant) is indeed critical. Such results will be of importance in the design of efficient nanoparticle foliar fertilisers, building material design and other applications were orientation can be easily manipulated.

## 2. Experimental

### 2.1. Materials

Suspensions of 0.01% w/w silica spherical particles (40–50 nm in diameter) were prepared by dilution of stock (20% w/w) Snowtex-20L (Nissan Chemical, USA) with ultrapure water. Water used in the experiments was freshly purified using a setup consisting of a reverse osmosis RIO's unit and an Ultrapure Academic Milli-Q system (Millipore, USA). Measurement of the 0.01% w/w Snowtex-20L suspension pH was not possible due to the low ionic strength of the Milli-Q water used for dilution. After addition of background electrolyte (KCl) the pH was measured as 5.6. All experiments were conducted without a background electrolyte.

Silicon wafer surfaces terminated with thermal silicon oxide layer (Silicon Valley Microelectronics, USA) were first cleaned ultrasonically (10 min in each acetone, ethanol and water), soaked for 15 min in a $5H_2O$:$1NH_4OH$:$1H_2O_2$ solution (RCA-SC1) at 75 °C , washed with copious amounts of water and then dried under a nitrogen stream. The hydrophilic silica surface was rendered hydrophobic by immersion into a 10 mM solution of n-octadecyltrichlorosilane (Sigma–Aldrich, Australia) in n-heptane (Sigma–Aldrich, Australia) for 10 s. The silanated surface was cleaned with n-heptane and acetone (AR grade). The advancing (110°) and receding (102°) contact angle of sessile water droplets were obtained using the PAT1 tensiometer (SInterface Technologies, Germany).

### 2.2. Methods

Drops (0.5 μL) of the colloidal suspension were dispensed (0.5–10 μL pipette, Eppendorf Research, Germany) onto the hydrophobic surface at ambient conditions (50–60% relative humidity, 23 ± 1°) in the sessile configuration and immediately transferred to an enclosed chamber, in either the pendant or sessile position. Droplet evaporation was observed using a x10 objective (Nikon, Japan) and a progressive scan CCD camera (model XCD-SX910, Sony, Japan). A fiber light with diffuser was used to illuminate the drop from behind. Dimensional analysis of the droplet images was performed using an in-house Matlab code that automatically calculates the droplet dimensions.

After drying, each nanofluid deposit was imaged from a top view using an Eclipse TE2000-E inverted microscope fitted with a Plan Fluor 40x objective and a PC-based microscope camera (Nikon, Japan). Cross-sectional profiles of each deposit were taken using a Dektak 150 Profilometer (Veeco, USA) at minimum contact force (1 mg). The underside of the deposits was exposed by placing a small piece of carbon tape (Proscitech, Australia) over the deposit and then removing. The deposit adhered to the carbon tape and was imaged using a scanning electron microscope (JEOL JSM-6300 SEM).

## 3. Results and discussion

### 3.1. Deposit analysis

A significant difference in the deposit pattern is observed between the sessile and pendant drop configurations. A coffee ring surrounding a thin particle layer formed in the sessile droplet configuration (Fig. 1a) whereas a deposit consisting of a bump like feature with a faint ring on the deposit periphery formed in the pendant droplet configuration (Fig. 1b). Experiments were completed many times (>10) to confirm the general shape of the deposits. The deposit topography was confirmed by cross-sectional profiles of the sessile (Fig. 1c) and pendant (Fig. 1d) deposits with a profilometer.

Problems occurred with the cross-sectional profile of the sessile coffee ring deposit. Firstly, it was difficult to profile across the center of the deposit due to positioning problems. As the cross-section is not taken through the exact center, the coffee ring thickness is larger than that measured by top-view optical microscopy (Fig. 1a). A more significant problem was the stability of the coffee ring to the force of the profilometer tip. As shown in Fig. 2, the coffee ring of the sessile deposit was removed after analysis. However, the nanoparticle layer within the coffee ring remained. This resulted in erroneous data when the tip probed the coffee ring from within the ring to outside the ring, as shown by the red dotted data in Fig. 1c. The instability of the ring as it is probed from within the ring to outside the ring was observed for a number of different ring deposits. If the coffee ring was probed far from the center of the deposit the ring was stable in a number of cases. The bump deposit of the pendant drop was stable to the force of the probing tip.

The underside of the deposits was exposed by removing the deposits from the hydrophobic silica with carbon tape. The exposed underside of the sessile coffee ring and pendant bump deposit is shown in Fig. 3. The deposit was not perfectly preserved during removal, but large sections were still available for analysis. Both the sessile coffee ring and the pendant bump deposits have flat undersides, filled with particles. Complete cavities or "igloos", as shown by Sommer [14,15], are not present. However, the sessile coffee ring does appear to have an "overhang" or an incomplete "igloo", as shown in Fig. 3b. The "overhang" was not observed using the Profilometer (Fig. 1c) as the tip probed the top of the coffee ring. Such an "overhang" explains why the slope measured by the Profilometer on the inner side of the coffee ring is much steeper that the outer side, and may explain the instability of the coffee ring to the profiling tip as it probes from within the ring to outside the ring.

The significant alteration of the deposit pattern with surface orientation is not expected for small, slowly evaporating water droplets containing stabilized nanoparticles for three reasons:

(1) Droplet shape is constant with orientation: In the case of small drops the droplet shape will be identical regardless of position, that is, the droplet is not deformed by gravity, (Bond number $(Bo) \ll 1$), as found by others [16,17]. Thus diffusive evaporation, the resulting internal flows that form the deposit pattern and the dynamics of the contact line will be consistent with surface orientation. Results by Sommer [13] confirm that the deposits of smaller droplets are not influenced by orientation.

(2) Other internal flows are insignificant: For a slowly evaporating (i.e. medium to high humidity) water droplet the Marangoni flow is weak [18] and material flow induced by a temperature gradient pointing from the evaporation cooled water-vapor interface to the warmer water–solid interface [13,19,20] is expected to be minimal (smaller drops also limit this effect [13]). Therefore, additional flows against/with gravity induced nanoparticle movement are not expected to be significant for the small water drops evaporated at medium humidity used in this study.

(3) The nanoparticles are very stable: If the nanoparticles are not stable, aggregation will produce deposit patterns dependant on the droplet position, as shown by Sandu and Fleaca