



# HOW DO COLLOIDAL DROPLETS EVAPORATE WHEN AT AN INCLINE?

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## 1. INTRODUCTION

Droplet evaporation and the associated coffee-ring effect are ubiquitous in everyday lives, from spilt milk or coffee in our kitchens, to spray cooling, coatings development and medical diagnostics [1]. A droplet on a hydrophilic surface (water contact angle  $<90^\circ$ ) evaporates mainly from the edges of the droplet with the apex of the droplet exhibiting the lowest evaporation rate as described in the seminal work by Deegan and co-workers [2]. They also showed that this enhanced flow at the periphery of the drop resulted in a stronger internal flow to replenish the evaporated liquid which carries particles from the bulk to the periphery of the drop resulting in what is now known as coffee-ring pattern.

Due to the iniquitousness of this phenomenon both in nature and in application, research interest has since focused on this phenomenon in order to fully understand it and explore the different parameters that affect it. For example, heating the drops resulted in faster evaporation times [3], whereas lowering the ambient pressure led to perfectly crystalline deposit patterns [4]. More hydrophobic surfaces lowered the evaporation flux [5] and softer surfaces led to different evaporation regimes and patterns [6].

Nonetheless, the vast majority of the research to date focused on drops evaporating on horizontal surfaces in spite the numerous encounters in our daily lives with drops on inclined surfaces such as the windshield of a car or the photovoltaic arrays on our roofs. Only a small number of them has focused on the relationship between inclination angle and evaporation rate with contradicting findings [7-9]. In this work, we chose large aqueous colloidal drops, beyond the capillary length of water, in order to maximise the influence of gravity on their shape and hence evaporation kinetics and the coupled deposit formation mechanism. We found that increasing the inclination slows the evaporation time and elongates the resulting deposit pattern with large particulate accumulation towards the thinner side of the drop. This accumulation could be attributed to the majority of the contact line shows a higher contact angle at the front and hence should both slow the evaporation and slow the outward fluid flow.

## 2. EXPERIMENTAL METHODOLOGY

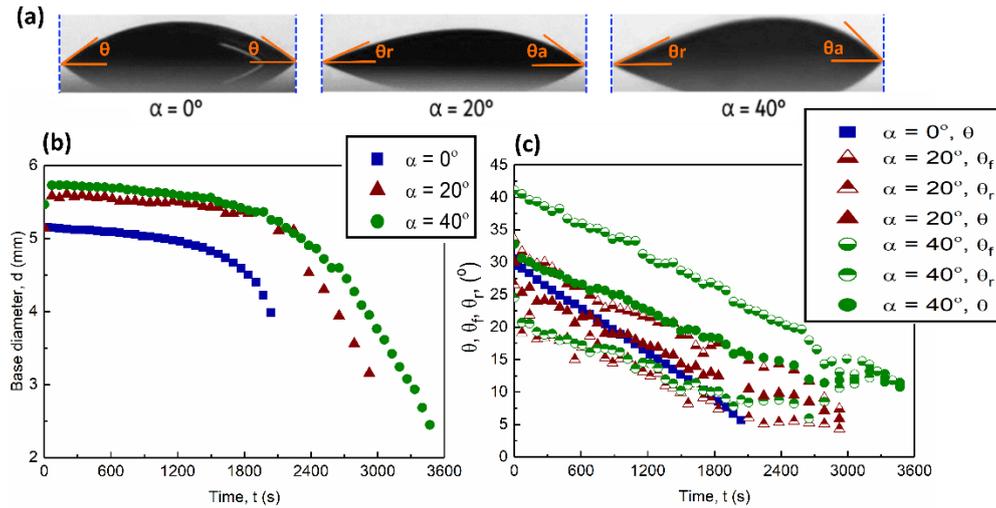
1  $\mu\text{m}$  polystyrene colloidal aqueous suspensions (Polybead, Polysciences, US) were diluted to desired concentration of 0.1% w/w in deionised water. Prior to use, the suspension was sonicated for 10 minutes to ensure uniform dispersion. Smooth hydrophilic glass slides were ultrasonically cleaned consequently in deionised water and ethanol for 10 minutes and dried under a stream of compressed air. 9  $\mu\text{l}$  droplets were gently deposited by a micropipette onto substrates with the inclination angles,  $\alpha = 0, 20, 40^\circ$ . Experiments were conducted under ambient conditions and a CCD camera and a back light were employed to capture the shadow side-view images of drying drops. The evolution of drop profiles (i.e., base diameter, contact angle, volume) were computed a drop shape analysis software (DSA4, Krüss, Germany). Resulting coffee-ring patterns were imaged using an optical microscope.

## 3. RESULTS AND DISCUSSION

The drops are placed in inclinations,  $\alpha = 0, 20, 40^\circ$ , resulting in elongation of their shape as shown in Figure 1a. Hence, we need to consider their advancing and receding front characterised by the advancing and receding angles,  $\theta_a$  and  $\theta_r$  respectively. The temporal evolution of the profile of each drop is presented in Figure 1b,c in terms of base diameter and contact angle. It is readily apparent that in all

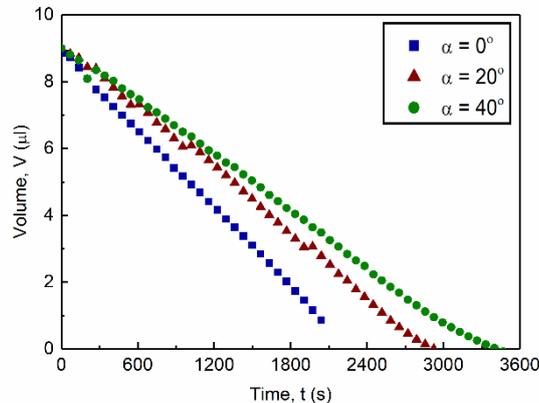
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cases the drops evaporate under the constant radius regime as is readily apparent in Figure 1b,c, by the constant diameter across the evaporation process with simultaneous constant decrease in contact angle [10]. At the same time, an initial spreading period can be identified in the base diameter in Figure 1b for the 20 and 40° cases due to the action of gravity upon deposition and until the drops reach their equilibrium state. Additionally, we observe in Figure 1c that in both inclined cases the mean contact angle,  $\theta$  (solid brown and green symbols), value lies between  $\theta_a$  and  $\theta_r$  (partly filled brown and green symbols respectively). It is also clearly discernible that the evaporation time of each drop is dependent on the inclination angle, which we focus next.



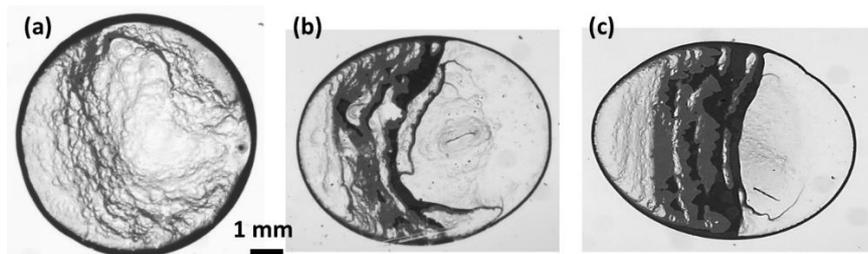
**Figure 1:** (a) Initial snapshot of a 0.1% microspheres drop evaporating at 0°, 20° and 40° inclination with corresponding mean contact angle,  $\theta$ , receding contact angle,  $\theta_r$ , and advancing contact angle,  $\theta_a$ . Evolution of the same drops over time: (b) base diameter and (c)  $\theta$ ,  $\theta_r$  and  $\theta_a$ . Blue, brown and green symbols show 0°, 20° and 40° inclinations, respectively.

Figure 2 shows the dependence of evaporation time on the inclination angle. In particular, as the angle increases from horizontal to 20°, the evaporation time increases by 43%. Further increasing the inclination to 40°, the evaporation time increases a further 18%. This increase in evaporation time should be attributable to the non-uniform distribution of evaporation flux along the three-phase contact line of the drops. In fact, the inclination of the drops leads to the elongated profiles shown in Figure 1a which in turn result in a longer length of three-phase line (or part) of the drop under the higher advancing angle  $\theta_a$  and the resulting lower evaporation rate. This finding is in agreement with previous reports of an inversely proportional relationship between evaporation time and contact angle of the drop [5].



**Figure 2:** Evolution of drop volume over time for drops at 0, 20 and 40° inclination (blue, brown and green respectively).

The elongation of the drops due to the inclination also affected the resulting deposit patterns, as seen in Figure 3. The patterns start with a symmetrical one at 0° inclination and a typical ring-stain deposit at the periphery with some build-up to the interior (Figure 3a). Inclining the surface to 20° and 40° led to elongated patterns (Figure 3b,c), in line with elongated drop shape previously. Additionally, in the elongated deposits higher particle accumulation was found at the receding side of the drop and less accumulation to the advancing front. This behaviour should be attributed to the enhanced evaporation flux at the receding side and the weakened flux at the advancing side due to the lower and higher contact angles. Some additional wetting fronts can be clearly identified in both these cases as striped regions due to perhaps the motion of the receding front after it depinned during the evaporation process and depositing and re-arranging the particulate accumulation trapped in the thinner part of the drop.



**Figure 3:** Deposit patterns left behind the evaporation of 9  $\mu$ l aqueous drops containing 1  $\mu$ m microspheres at (a) 0°, (b) 20° and (c) 40° inclinations. In every image right side corresponds to advancing side.

#### 4. CONCLUSIONS

We report on the influence of substrate inclination on the evaporation kinetics and deposit formation mechanism of evaporating colloidal drops. We showed that a small increase of the inclination angle results in substantial decrease in the evaporation time of the drops by elongating its shape and leading to a receding and an advancing front (thinner on the top and thicker on the bottom of the drop) which in turn result in different evaporation rates at the two sides. This difference in evaporation rates was verified by the deposit patterns with the majority of the particulate located toward the receding front as a result of the enhanced evaporation rate and the linked liquid flow from the centre of the drop to its periphery. These results should be useful in a plethora of applications from painting and printing self-cleaning surface that are not always in the horizontal orientation as has been the consensus in the experimental works so far.

#### REFERENCES

- [1] D. Zang, S. Tarafdar, Y. Y. Tarasevich, M. Dutta Choudhury, and T. Dutta, Evaporation of a Droplet: From physics to applications, *Physics Reports*, 804,(2019), 1-56
- [2] R. D. Deegan, O. Bakajin, T. F. Dupont, G. Huber, S. R. Nagel, and T. A. Witten, Capillary flow as the cause of ring stains from dried liquid drops, *Nature*, 389,(1997), 827-829
- [3] M. Parsa, S. Harmand, and K. Sefiane, Mechanisms of pattern formation from dried sessile drops, *Advances in Colloid and Interface Science*, 254,(2018), 22-47
- [4] A. Askounis, K. Sefiane, V. Koutsos, and M. E. R. Shanahan, The effect of evaporation kinetics on nanoparticle structuring within contact line deposits of volatile drops, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 441,(2014), 855-866
- [5] K. Gleason, H. Voota, and S. A. Putnam, Steady-state droplet evaporation: Contact angle influence on the evaporation efficiency, *International Journal of Heat and Mass Transfer*, 101,(2016), 418-426
- [6] Y. Chen *et al.*, On the Effect of Substrate Viscoelasticity on the Evaporation Kinetics and Deposition Patterns of Nanosuspension Drops, *Langmuir*, 36,(2020), 204-213
- [7] J. Y. Kim, I. G. Hwang, and B. M. Weon, Evaporation of inclined water droplets, *Scientific Reports*, 7,(2017), 42848
- [8] M. L. Timm, E. Dehdashti, A. Jarrahi Darban, and H. Masoud, Evaporation of a sessile droplet on a slope, *Scientific Reports*, 9,(2019), 19803
- [9] W. Qi, J. Li, and P. B. Weisensee, Evaporation of Sessile Water Droplets on Horizontal and Vertical Biphobic Patterned Surfaces, *Langmuir*, 35,(2019), 17185-17192
- [10] A. Askounis, K. Sefiane, V. Koutsos, and M. E. R. Shanahan, Structural transitions in a ring stain created at the contact line of evaporating nanosuspension sessile drops, *Physical Review E*, 87,(2013), 012301