LANGMUIR
Comment
Cite This: Langmuir 2019, 35, 9991−9993
pubs.acs.org/Langmuir

Reply to "Comment on 'Patterns in Drying Drops Dictated by Curvature-Driven Particle Transport'"

ABSTRACT: Hodges and Tangparitkul (Hodges, C. S.; Tangparitkul, S. M. *Langmuir* **2019**, *35*, doi: 10.1021/acs.langmuir.9b01442) in their Comment on "Patterns in Drying Drops Dictated by Curvature Driven Particle Transport" argue that the coffee-eye deposits in dried pendant drops can also be formed if the particles or particle clusters in the drying drop are large enough to sediment during the course of evaporation. In our reply to this comment, we compare these two different mechanisms, namely, gravity settling and curvature-driven interfacial migration of particles in the drying particle-laden drops, with an aim towards placing them in a correct perspective.

Hodges et al.[1] performed experiments to demonstrate that the drying pendant drops containing colloids leave a "coffee-eye" (i.e., the accumulation of particles in the center of the dried deposit). They explained that such a deposition is due to the gravitational settling of the particles. They conducted pendant drop drying experiments using droplets containing charge-stabilized (zeta potential = −30 mV) spherical silica colloids of two different sizes (100 and 500 nm in diameter) at 23 °C and 30% relative humidity. The experiments were conducted by drying drops of 10 μL volume on a neutral wetting substrate ($\theta = 90°$). The final deposits from drying experiments were characterized by optical and atomic force microscopy (AFM). The measurements showed that there is a gradual change in the deposit height from the edge to the center, with the height being maximum in the center. The authors attribute the formation of these deposits to gravity settling of the particles. We agree with the fact that the gravity settling of particles, if prominent, will lead to the central deposition, which is also reported by Hampton et al.[2] However, as we discuss below, in the work of Hodges and Tangparitkul[1] it can be argued that the central deposit is not solely due to the gravity settling of particles for the following reasons:

(1) Hodges et al.[1] state that the nanoparticles in the aqueous dispersion drops used in drying experiments have no interfacial activity (surface tension = 72.4 mN/m for 100 nm particles and 72.3 mN/m for 500 nm particles). To confirm the surface-active nature, it is necessary to measure the evolution of surface tension during drying experiments, which is much more complex. The temporal evolution of surface tension as a function of time can be measured using pendant drop tensiometry. In such experiments, the adsorption of particles at the interface and hence their surface activity is dictated by the diffusivity of particles and the surface-charge-dictated energy barrier.[3] In the evaporation experiments, the drop surface−air interface that descends during drying invariably captures the particles; therefore, irrespective of particle size and surface chemistry all particles are expected to be trapped by the interface.

(2) The other concern is the large volume of the drop (10 μL) used for the drying experiments. Typically, such large drops, unlike much smaller ones, are more susceptible to gravity deformation. Therefore, curvature-driven migration can be more prominent in the reported experiments.

(3) The distinction between the coffee-ring-like and coffee-eye-like deposits is not evident either from the optical microscopy images or from the deposit profiles. The deposits from both smaller and larger particles show a gradual rise in the height from the edge to the center. Therefore, the argument that gravity settling leads to coffee-eye deposits is not substantiated. Moreover, there has been no comparison with deposit patterns from the drying of drops in sessile configurations and other orientations. Paradoxically, authors claim that "the deposit of 100 nm particles agrees with the structure shown by Hampton et al.",[2] wherein gravity settling is shown to dictate the pattern formation.

We further present an analysis of patterns formed by evaporating drops containing spherical polystyrene particles of 3 μm and 70 nm diameters on substrates of different wettability and orientation to demonstrate the role of curvature-driven migration of particles, even in instances where the particles are small and not affected by gravity settling. To this end, we present the results of drying experiments (1) by considering drops containing 3 μm particles when all parameters except wettability is varied and (2) by considering drops containing 70 nm particles when all parameters except substrate orientation is varied.

The deposit pattern shown in Figure 1a1 is obtained by drying 1 μL drops containing charge-stabilized (zeta potential ≈ −92 mV) spherical polystyrene particles (sulfate latex) of 3 μm diameter in a pendant configuration. The corresponding two-dimensional surface profile (contour GT optical profiler, Bruker) in Figure 1a2 captures the presence of the central dome, unlike the formation of the usual coffee-ring when the drops are dried in a sessile configuration. Note that these drying experiments are performed on a neutral wetting substrate (i.e., the aqueous dispersion placed on the substrate makes a contact angle of $\theta = 90 \pm 2°$). All conditions being identical, when pendant drops are dried on substrates with $\theta = 40 \pm 2°$, the central dome completely disappears. Instead, a deposit with particles accumulated as a wider ring near the periphery, which is shown in Figure 1b1,b2. However, if the central dome observed in Figure 1a1 is due to the gravity settling of particles, then a similar central dome is expected to form in Figure 1b1. Therefore, the formation of the central dome in Figure 1a1

Received: July 10, 2019
Published: July 10, 2019

DOI: 10.1021/acs.langmuir.9b02139
Langmuir 2019, 35, 9991−9993

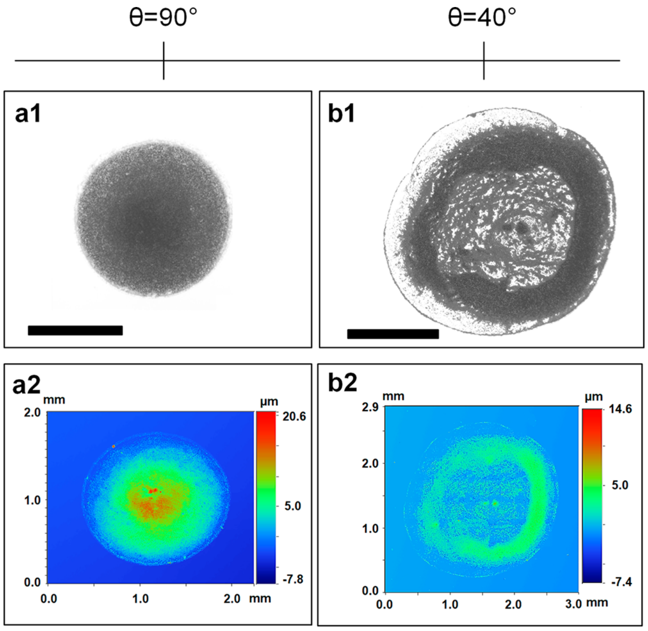

Figure 1. Comparison of patterns formed by drying 1 μL drops in the pendant (also called hanging drop) configuration. The drops contain spherical polystyrene particles of 3 μm diameter, and the drops are dried on substrates of different wettability: a1 and a2 correspond to $\theta = 90 \pm 2°$ and b1 and b2 correspond to $\theta = 40 \pm 2°$. The images in a1 and b1 are obtained by performing optical microscopy of the dried deposit patterns. The two-dimensional surface profiles that capture the deposit height are shown in a2 and b2. The scale bars in a1 and b1 correspond to 1 mm, and the color bars that appear in the surface profiles in a2 and b2 show the deposit height in μm. Panels a1 and a2 are reproduced with permission from ref 4. Copyright (2019) American Chemical Society.

appears to be mainly due to the curvature-driven migration of particles which has already been reported,[4] and it becomes prominent with the decrease in substrate wettability (or the increase in the contact angle of the drop).

Now, we move on to present deposit pattern obtained by drying of 1 μL drops containing charge-stabilized (zeta potential, $\sim 38 \pm 2$ mV) spherical polystyrene particles (amidine latex) of 70 ± 5 nm diameter in sessile, pendant, and vertical configurations. The drying experiments are performed on an acetone-cleaned glass substrate. On these surfaces, the aqueous dispersions that are deposited are observed to form a drop that takes the shape of a spherical cap with a contact angle of $\theta = 40 \pm 2°$. All experiments were carried out at $64.8 \pm 1.2\%$ relative humidity and a temperature of 24.94 ± 1.16 °C. From the patterns in Figure 2a1,b1 obtained by drying drops, respectively, in sessile and pendant configuration, it can be concluded that the deposits are on average axisymmetric and coffee-ring-like. The surface profiles corresponding to microscopy images in Figure 2a1,b1 are shown respectively in Figure 2a2,b2. Therefore, in line with the deposits formed when pendant drops with 3 μm particles are dried on substrates of the same wettability ($\theta = 40 \pm 2°$), the region where the particles are concentrated moves closer to the contact line, giving rise to coffee-ring deposits. We believe that there are two aspects of gravity that are important in the drying drop problem: (1) the gravitational force on the particles and (2) the effect of gravity on the drop itself. The former influences the sedimentation of particles or the particle aggregates, hence affecting the distribution of particles in the final deposit. The latter contributes to drop deformation and brings about the role of interface curvature, which is known to affect particle migration.[5] From the deposit patterns and the corresponding surface profile shown in Figure 2c1,c2, it is clear that the distribution of 70 nm particles is not axisymmetric (i.e., the patterns do not exhibit angular symmetry when the drops are dried on a vertical substrate). Similar to our earlier results,[4] there is a relatively smaller concentration of particles on the receding side of the drop and more particles are deposited at the advancing side of the drop. This is clearly not due to the effect of gravity on the particles. The subtle changes in the drop shape due to gravity modifies the fluid flow pattern inside the drop and along the interface (drop surface). Therefore, the curvature-driven migration depending on several parameters such as the substrate wettability, drop orientation, competition between gravity settling, and interfacial capture of particles and possibly particle concentration can lead to intriguing deposits patterns, which needs to be further investigated.

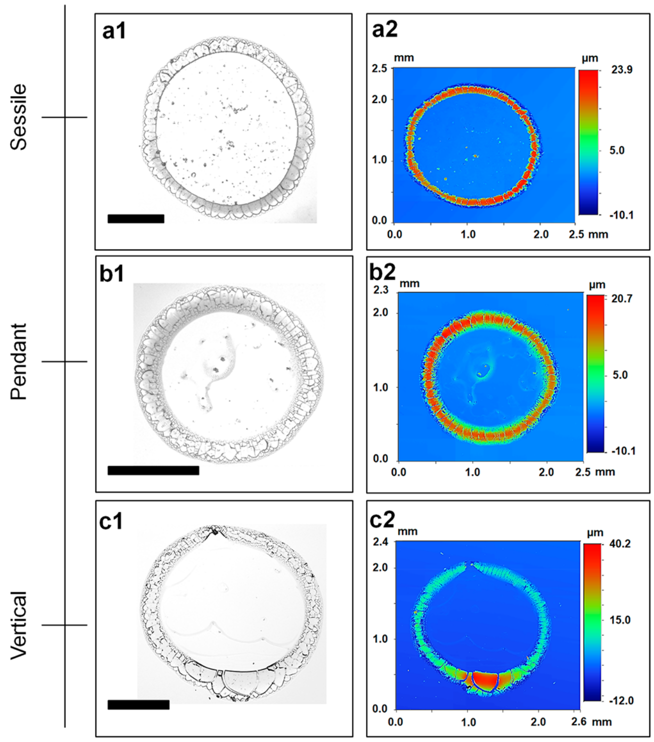

Figure 2. Comparison of patterns formed by drying 1 μL drops in sessile, pendant, and vertical configurations. The drops containing spherical polystyrene particles of 70 ± 5 nm diameter are dried on substrates with $\theta = 40 \pm 2°$. The micrographs in a1, b1, and c1 are recorded using an optical microscope, and the surface profiles in a2, b2, and c2 depict the height of the deposits. The scale bars in a1, b1, and c1 correspond to 1 mm, and the color bars that appear in the surface profiles in a2, b2, and c2 show the deposit height in μm.

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DOI: 10.1021/acs.langmuir.9b02139
Langmuir 2019, 35, 9991−9993

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Notes

The authors declare no competing financial interest.

REFERENCES

(1) Hodges, C. S.; Tangparitkul, S. M. Comment on "Patterns in Drying Drops Dictated by Curvature-Driven Particle Transport". *Langmuir* **2019**, DOI: 10.1021/acs.langmuir.9b01442.

(2) Hampton, M. A.; Nguyen, T. A.; Nguyen, A. V.; Xu, Z. P.; Huang, L.; Rudolph, V. Influence of surface orientation on the organization of nanoparticles in drying nanofluid droplets. *J. Colloid Interface Sci.* **2012**, *377*, 456−462.

(3) Dugyala, V. R.; Muthukuru, J. S.; Mani, E.; Basavaraj, M. G. Role of Electrostatic Interactions in the Adsorption Kinetics of Nanoparticles at Fluid−Fluid Interfaces. *Phys. Chem. Chem. Phys.* **2016**, *18*, 5499−5508.

(4) Mondal, R.; Semwal, S.; Kumar, P. L.; Thampi, S. P.; Basavaraj, M. G. Patterns in Drying Drops Dictated by Curvature-Driven Particle Transport. *Langmuir* **2018**, *34* (38), 11473−11483.

(5) Cavallaro, M., Jr.; Botto, L.; Lewandowski, E. P.; Wang, M.; Stebe, K. J. Curvature-driven capillary migration and assembly of rod-like particles. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *108*, 20923−20928.

DOI: 10.1021/acs.langmuir.9b02139
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