Supporting Information

Experimental set-up, temperature measurements and roughness characterization

Figure S1 shows the experimental setup for heating the substrate. Substrates are attached to the heater by a thin layer of thermal grease of thermal conductivity 1.7 W/mK. A small electronic heater of size 40×40×2.4 mm allows us to carry out experiments under a microscope, and the size of the glass slide is 76×25×1.1 mm (Figure S1a). A small rectangular area of 20×15 mm at the center of the substrate is used for temperature measurements and drying experiments. Before each experiment, the temperature of the substrate is determined using a resistance thermal detector (RTD) Pt100 (PTFN, Sensotherm, Germany), with temperature coefficient of resistance α=0.0038 and size 5.0×1.6×1.1mm. The temperature is measured before each drying experiment; the substrate must be clean, so that no thermal grease was used for the contact between the detector and the substrate. Instead, contact is made by a mechanical way: the detector is pressed onto the top surface of the substrate by a thin rod covered by rubber. Each temperature is recorded once it is stabilized – when the detector signal does not vary more than 0.5°C for five minutes. Temperature is measured at the top of the substrate, at four corners and at the center (A, B, C, D, E) of the central area. Temperatures between the five points are found to vary within $\pm 1°\mathrm{C}$. Hence for a drop with a diameter of 4 mm, temperature differences remain smaller than 0.2°C. The device is placed under an optical microscope to follow the drying process and the trajectory of the particles.

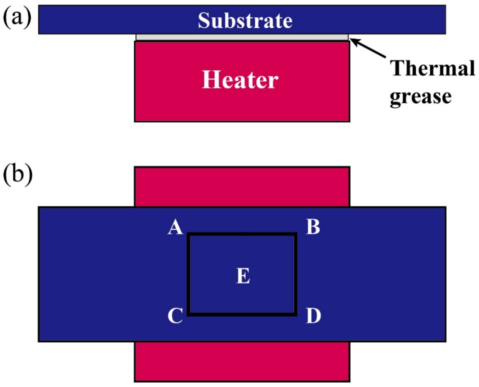

Figure S1. Experimental set-up for heating. (a) Side view. (b) Top view showing the locations where temperature is measured.

We characterized the roughness of the different samples (glass, polystyrene, PMMA) used in our experiments. An area of 100×100 µm on the substrates was randomly picked and probed by an AFM (NTEGRA Aura, NT-MDT, Russia) at a speed of 60 µm/s in tapping mode. The

RMS roughness of glass, polystyrene and PMMA substrates was found to be 3.4 nm, 20.1 nm and 12.3 nm, respectively. We display in Figure S2 typical AFM images corresponding to these different samples.

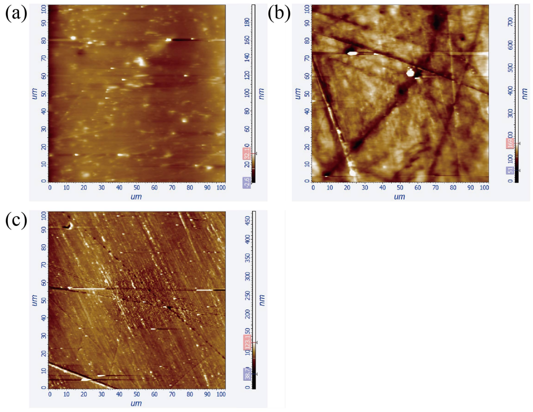

Figure S2. AFM pictures showing the surface roughness of the substrates used in our experiments: (a) Glass slide. (b) Polystyrene. (c) PMMA.

Particles gathering at the surface

To see whether particles are gathering at the liquid-vapor interface, a needle is used to scratch the surface of the drop. When illuminated from aside, particles scatter the incident light and appear white. As shown in Figure S3, the scratched area is black, which means no particles there and confirms that particles sit at the liquid-vapor surface of the drop.

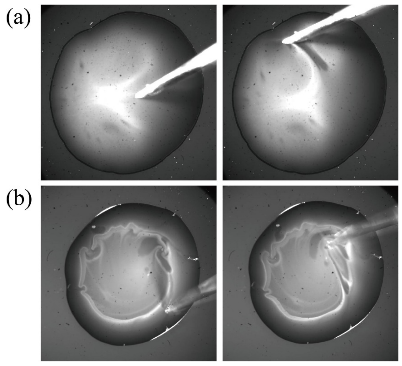

Figure S3. Scratching the droplet surface with a needle at different substrate temperatures. (a) $T = 30°\text{C}$. (b) $T = 60°\text{C}$. Scratched area becomes black, which indicates particles (white) sit at the drop surface.

Influence of substrate thickness and thermal conductivity

In order to investigate the influence of the substrate thickness and thermal conductivity on the stain pattern, we tested glass of thermal conductivity 0.85 W/mK, 0.2mm, 1mm, 3mm thick, respectively; polystyrene of thermal conductivity 0.3 W/mK, 1 mm thick; and PMMA of thermal conductivity 0.2 W/mK, 5mm thick are used as substrates. All of these substrates are much smaller than the hot plate. Temperatures at the top of the substrates are constant within ±1°C. Water droplets with uniformly dispersed polystyrene (PS) spheres of diameter ~100 nm and concentration of 2.5 mg/mL are used.

Figure S4 shows the deposition pattern on such substrates at 70°C. As can be seen, the stains on glass of various thicknesses are nearly the same. And for 1mm-thick substrates of different thermal conductivities, little difference in the stain is observed. Deposits all form an “eye stain” - we just note that a larger pupilla is found on PMMA.

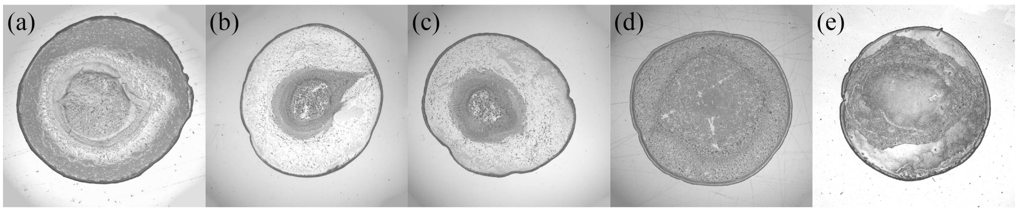

Figure S4. Stains on substrates of different thickness and thermal conductivity. (a) 0.2 mm thick glass. (b) 1 mm thick glass. (c) 3 mm thick glass. (d) 5 mm thick PMMA. (e) 1 mm thick plastic.

Influence of the size and the charge of particles

To see whether and how the size and charge of the particle influence the final stain, droplets with 1μm diameter particles at a concentration of 2.5 mg/mL (that is, the same concentration as for the 100 nm particles) are dried on glass at T = 70°C. As shown in Figure S5a, the particles are also caught at the surface, and then brought towards the central area. They concentrate in a larger area compared to that with 100nm particles, which remains to be quantitatively understood.

To investigate the influence of the surface charge, droplet with 100nm particles at a concentration of 2.5mg/mL also containing KOH (0.01M) are dried on glass at T = 70°C. As shown in Figure S5b, the droplet dries with the same mechanism: particles are first caught at the liquid-vapor interface, then brought toward the center by an inward surface flow. The water film breaks up near the ring, and the particles concentrated in the central area form a central stain. It is observed that the central stain is larger when KOH is added to the solution. The inner white area is believed to be KOH, which precipitates at the end of the drying process. According to Bhardwaj[1], KOH increases the surface charge of the particles, and larger repulsive forces between particles might favor larger central stains.

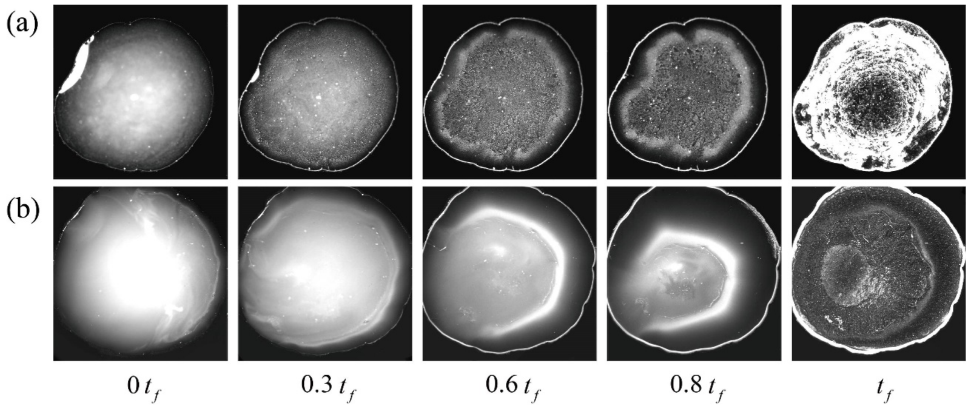

Figure S5. Influence of size and surface charge of the particles. (a) Drying process of a 2.5µL water droplet with 1µm diameter PS spheres at a concentration of 2.5mg/mL. (b) Drying process of a 2.5µL KOH solution (0.01M) droplet with 100nm diameter PS spheres at a concentration of 2.5mg/mL. Substrate temperature is 70°C in both experiments.

Reference

1. Bhardwaj, R.; Fang, X.; Somasundaran, P.; Attinger, D. Self-assembly of colloidal particles from evaporating droplets: role of DLVO interactions and proposition of a phase diagram. *Langmuir* **2010,** 26, 7833-7842.