Supplementary information

On the origin and evolution of depletion zone in coffee stains

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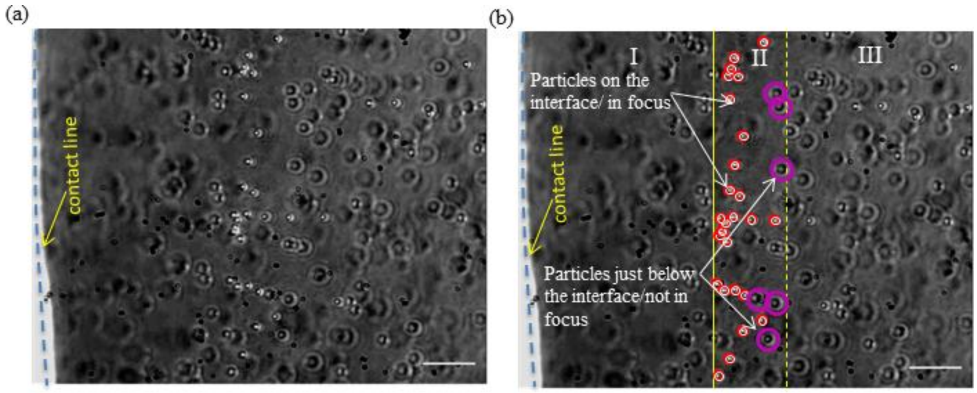

Figure S1. (a) Optical microscopy image of the interfacial area near the contact line of an evaporating composite colloidal particle laden droplet. Only few particles are in focus and are visible as bright white spots. (b) Microscopy image in which the particles which are 'in and out of focus' are identified and labeled. It is evident that only a thin strip of area marked as region-II within the yellow rectangle, is in focus, where particles are visible as bright white spots. Using a simple Matlab algorithm, these particles are identified and are encircled in red. Some particles which are not in focus within the selected strip are manually identified and encircled in magenta. These particles are situated just below the water-vapor interface. Particles in region-I lie below the Plane of Focus of the microscope. Therefore no particles are in focus within region-I. Few particles in region-III are in focus. However, these particles are present in the bulk of the droplet, and not along the water-vapor interface. Therefore, only those particles which are both in focus, and present along the water vapor interface are identified using the Matlab algorithm, by restricting the region of particle identification, only to region-II. Stitching 7-8 such strips of area regenerates approximately 141 x 105 µm area of the interface near the contact line. Scale bars on the microscopy images correspond to 20 µm.

Parameterized Young-Laplace equation

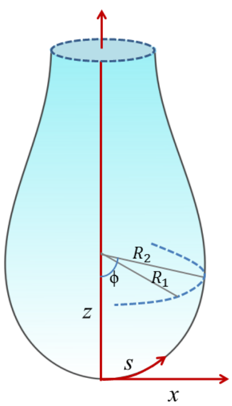

Figure S2. Schematic representation of an axisymmetric pendant drop

Schematic representation of a pendant droplet is shown in figure S2. At equilibrium, a pendant drop obeys Young-Laplace equation, given by Eq.1. In terms of the parameters *s* and ϕ, which represents the arc length and the tangent angle respectively, Young-Laplace equation transforms to a set of first order differential equations given by Eq. 2 - 4, with boundary conditions given by, $\bar{x} = 0$, $\bar{z} = 0$, $\phi = 0$ at $\bar{s} = 0$ where the bar above the parameters indicate that they are scaled by R_0, the radius of curvature at the apex of the pendant drop to render all the parameters dimensionless [1].

$$\Delta P = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \tag{1}$$

$$\frac{d\phi}{d\bar{s}} = 2 - \frac{sin\phi}{\bar{x}} - B_0\bar{z} \tag{2}$$

$$\frac{d\bar{x}}{d\bar{s}} = cos\phi \tag{3}$$

$$\frac{d\bar{z}}{d\bar{s}} = sin\phi \tag{4}$$

$$B_0 = \frac{\Delta\rho g R_0^2}{\gamma} \tag{5}$$

The shape of the droplet is fitted with the parameterized Young-Laplace equation using ADVANCE software supplied by Krüss, GmbH Germany. The dimensionless quantity B_0, the Bond number, is deduced from the fit. From B_0, interfacial tension, γ is calculated using Eq.5, where $\Delta\rho$ is the density difference between the droplet and the surrounding medium, *g* is the acceleration due to gravity and R_0 is the radius of curvature of the droplet at the apex.

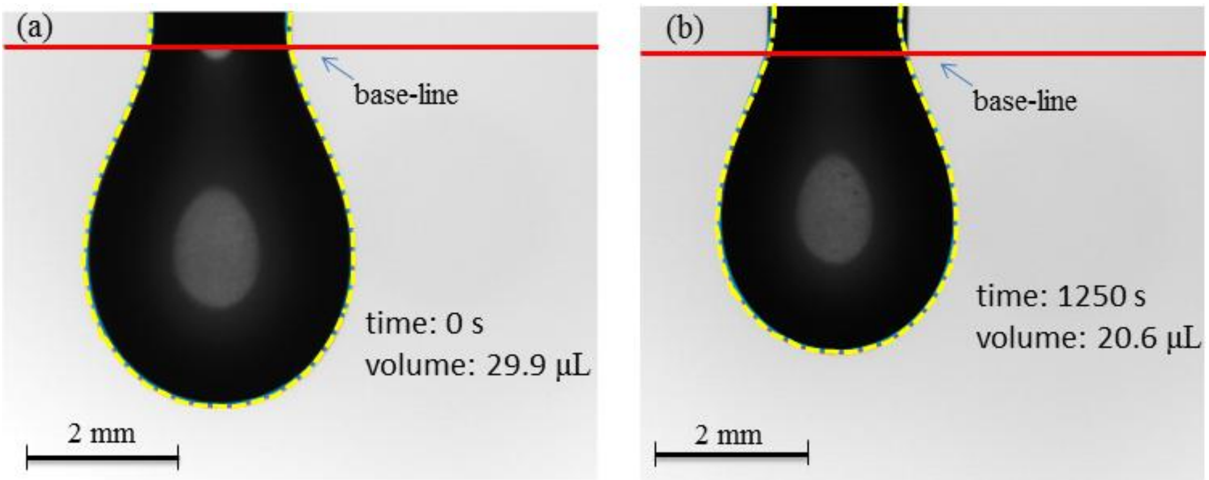

Figure S3. **Figure S3**. Pendant droplet of aqueous dispersion of a mixture of pNIPAM microgels (0.016 wt%) and PS particles (0.01wt%) suspended from the tip of a needle attached to an automatic syringe is shown (a) at initial time, t = 0 second and (b) at a later time, t = 1250 seconds. The drop shape profile is obtained using DSA 256E droplet shape analyzer from Krüss, GmbH, Germany. The yellow dotted line around the droplet corresponds to the best fit to the droplet shape, based on Young-Laplace equation. The horizontal red line passes through the tip of the vertical needle. It could be seen that the volume of the droplet shrinks due to evaporation of solvent with time. However, the shape of the droplet still remains considerably distorted from spherical shape, by the effect of gravity.

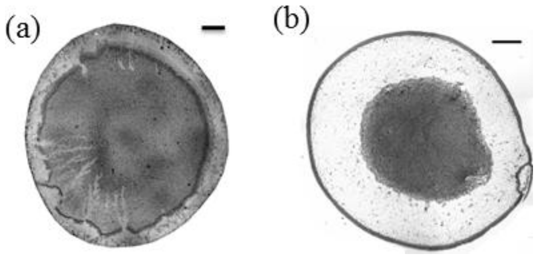

Figure S4. The optical microscopy images show the annular zone depleted of PS particles of different widths formed in the circular stains left behind by the evaporation of droplets containing 0.016 wt % pNIPAM microgels and different concentration of PS particles, (a) 0.005 wt % and (b) 0.025 wt %. The scale bars correspond to 500μm.

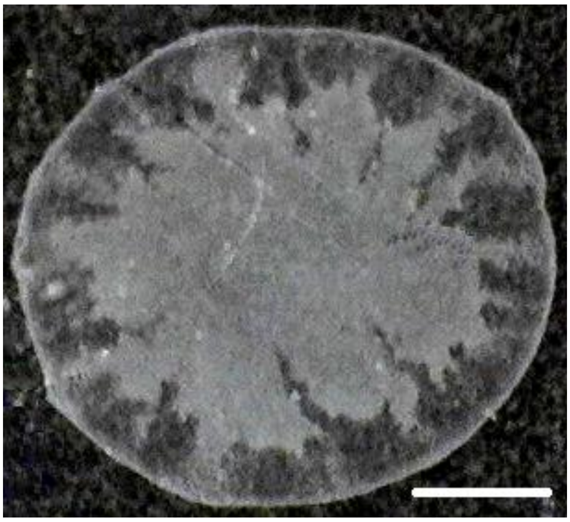

Figure S5. Flower-like deposition pattern formed by evaporation of a droplet containing a mixture of pNIPAM (0.016 wt %) and PS (0.025 wt %) particles. The depletion zone is irregular due to the non-uniform depinning of the contact line during the final stage of evaporation. The scale bar corresponds to 1 mm.

Reference:
[1] J. D. Berry, M. J. Neeson, R. R. Dagastine, D. Y. Chan and R. F. Tabor, *J. Colloid Interface Sci.*, 2015, **454**, 226–237.