Flow field induced particle accumulation inside droplets in rectangular channels - Supplemental Information

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1 Device Fabrication

Experiments were performed in microfluidic chips produced by standard soft-lithography[1]. In a first step, a negative photo resists (Su-8-100, MichroChem) was spin-coated on a silicon wafer, resulting in a resist film of $(100 \pm 5)\,\mu$m thickness that determines the channel height of the final device. SU-8 50, which is less viscous than SU-8 100, allows for lower film thickness and was used for devices with a smaller channel height, as used in Fig. 1 and Fig. 8. After transferring the channel geometry by UV-exposure and developing the resist, the resulting structure was used as a mold for device production. Liquid PDMS (Sylgard 184, DowCorning) was mixed at a ratio of base to curing agent of 10:1, poured onto the mold, cured and subsequently peeled off. The resulting PDMS slap containing the channel geometry was plasma bonded (Femto Plasma-Cleaner, Diener Electronic GmbH) to a glass slide to seal the channel after punching holes for inlets and outlets. Teflon tubing was inserted into these holes and inlets were connected to gas-tight glass syringes (Hamilton).

2 μPIV and fluorescence microscopy

Micro-Particle Image Velocimetry (μPIV) is a non-invasive, optical method to measure 2D flow fields on a micro-scale, first introduced by Santiago et al.[2]. In a μPIV experiment, the movement of small fluorescent tracer particles dispersed in the fluid and illuminated by two following laser pulses is imaged by a microscope and a camera. Subsequently, the two dimensional flow field in the image plane is calculated by cross-correlation of the recorded particle patterns. The optical setup consisted of an inverted microscope (Axio Observer Z1, Zeiss) with a motorized focal positioning system (motorized *z*-axis) and equipped with a 10x0.45 air objective (Apochromat, Zeiss). Images were recorded at different *z*-positions with a CCD camera (ImagerProX 2M, LaVision) coupled to the microscope by a 0.63 x camera adapter (Zeiss). Sample illumination was performed using a 532 nm DPSS-laser (LaVision, 2.72W) with pulse lengths ranging from 0.5 ms to 2 ms. The setup was computer controlled and PIV processing of the recorded images was performed using the DaVis 8.1.2 software package (LaVision). In μPIV experiments, fluorescent particles made of PS with a diameter of $1\,\mu$m (FluoroMax Red, Thermo Scientific) were mixed with the dispersed phase at a concentration of about $3.1 \cdot 10^9\,\mathrm{ml}^{-1}$.

One particular feature of μPIV is the use of volume illumination, which results in a typically unknown thickness of the measurement plane, known as Depth of Correlation (DOC), that depends on flow gradients, the tracer particles and the specific optical system. Estimating the DOC is crucial when planning experiments on complex 3D flows as present in droplets in rectangular channels, as the final measured velocity vector is a weighted average of all particle signals within the DOC. Recently, Hein et al.[3] published a method to precisely determine the DOC, considering out-of-plane gradients. Using this method and estimating the out-of-plane gradients from experimental data, the DOC in the present experiments was determined to vary between $11.2\,\mu$m and $15.3\,\mu$m. The vertical distance between measured planes was chosen accordingly.

The optical setup used to measure the flow field inside of elongated droplets by μPIV was also used to characterize the thickness of the surrounding oil films and the depth of the oil filled gutters in the corners of the channels. For these measurements, the continuous phase was dyed with Fluorescein27 at a concentration of 2 g/l. Focusing on the bottom of the channel, the fluorescence intensity then is a function of oil layer thickness. Calibration measurements performed on oil-filled channels of heights ranging from $11\,\mu$m to $68\,\mu$m indicate a linear increase of fluorescence intensity with oil layer thickness. However, the presence of the curved droplet interface, the channel walls and the second oil-filled gutter are expected to influence the measured intensities, especially when determining the gutter height next to the channel walls, cf. Fig. 4b. Thus, we refrain from converting the measured fluorescence intensities into absolute height values, although converted gutter heights and oil film thickness surrounding the droplet quantitatively agree with theoretical predictions[4]. Instead, the data in Fig. 4 is given in intensity counts and solely used to indicate changes of the droplet shape with increasing *Ca*.

The droplet motion through the field of view poses additional complexities when measuring both the flow fields as well as the fluorescence intensity of the oil phase that determines the height of the surrounding oil films. To reduce the

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effect of outliers in the instantaneous flow fields calculated by DaVis, a custom matlab script was used to perform averaging over several measured droplets. First the droplet velocity was subtracted from the measured flow fields to transform to the co-moving frame of reference of the droplet. To account for experimental fluctuations of droplet length, each vector field was superposed by a grid of (45x11) boxes. All vectors inside the same box were averaged, thus creating velocity fields of a given size and a typical spacial resolution of (30x30) μm. In a next step these velocity fields of uniform size were averaged for each measured droplet velocity and each measurement plane. Thus for each measured plane the x and y components of the flow velocity were determined, whereas the out-of-plane component is not accessible with the available μPIV-system. The same averaging procedure with a grid of (446x163) boxes was used for statistical analysis of the fluorescence intensity distribution of the surrounding oil layers. Profiles in Fig. 4 and Fig. 6 were subsequently extracted from the averaged data. $v_{rim}(x)$ was averaged over the boxes at the droplet interface on both sides. The fluorescence intensity determining the gutter height was averaged over three boxes on each side of the droplet about 9 μm from the estimated position of the channel sidewalls. Subsequently, a smoothing over the next 10 neighbors was used to reduce noise in the fluorescence signals.

References

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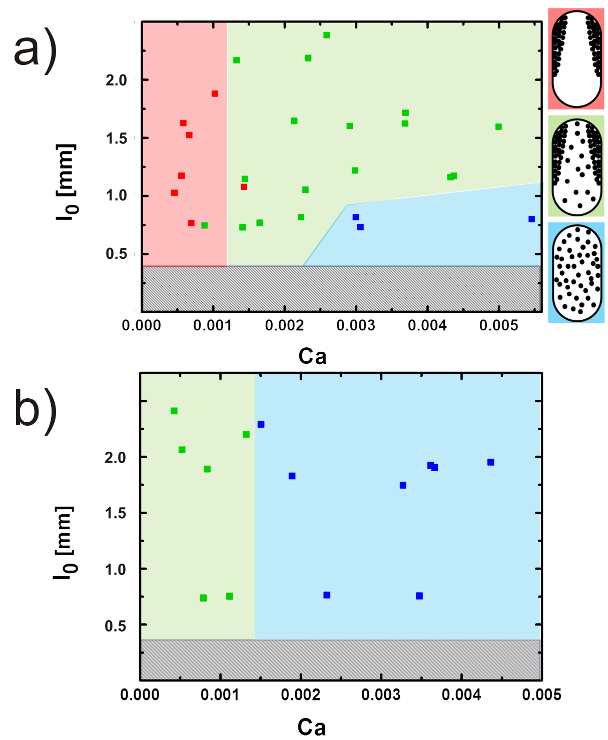

SI 1 'Phase-like' diagrams of particle accumulation for a) silica particles (Ø5 μm) and b) PS particles(Ø10 μm) within water droplets surrounded by n-hexadecane. 2 wt.% Span80 were added to the continuous phase. Sketches on the right depict the 'accumulation', 'intermediate' and 'mixing' regime and are shaded in the color of the corresponding phase.