RESEARCH ARTICLE

Manipulation of single sub-femtoliter droplets

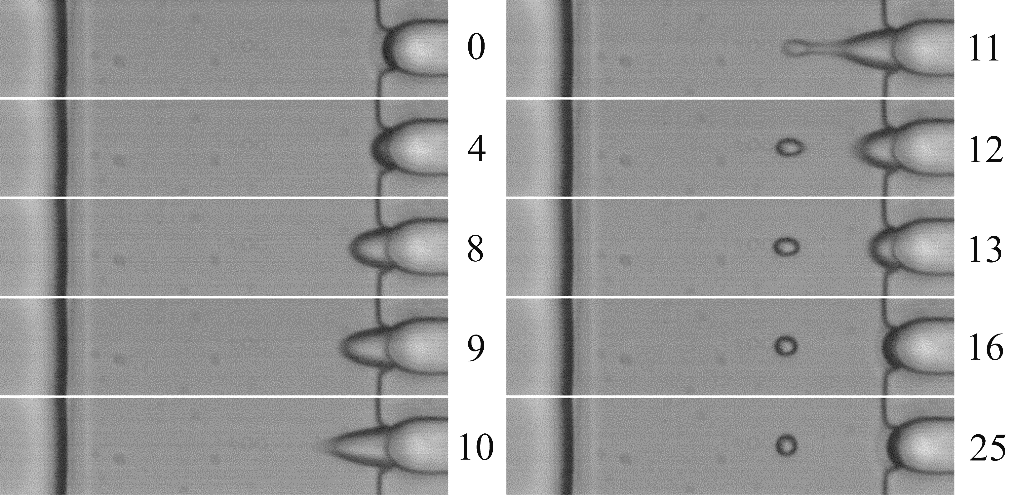
Manipulation of Single Sub-Femtoliter Droplets via Partial Coalescence in a DC Electric Field: Supplementary Material

Mostafa Shojaeian1 and Steffen Hardt1\*

1Fachbereich Maschinenbau, Fachgebiet Nano- und Mikrofluidik, Technische Universität Darmstadt, 64287 Darmstadt, Germany

**1. Droplet generation**

Droplets were generated in the microchannel by applying a voltage pulse between the side channels. Owing to the electric field lines converging at the liquid-liquid menisci, the electric field strength is higher at the narrower side channel. The capillary pressure, however, is dominated by the depth direction (channel depth 10 µm), which yields comparable capillary pressures in the narrower and the wider side channels. As a result, in the parameter space of pulse amplitudes and durations a domain can be identified in which electrohydrodynamic droplet production solely occurs at the narrower side channel. Typical pulse amplitudes and durations are 400 V and 10 ms. Figure S1 shows exemplary time-lapse images of the droplet generation.



***Figure S1****. Time-lapse images of the on-demand production of a water droplet using a voltage of 400 V and a pulse duration of 10 ms. The numbers next to the individual frames denote the time in milliseconds.*

**2. Fabrication of microfluidic device**

The microfluidic chip was fabricated using the soft lithography protocol. First, a SU-8 photoresist on a silicon wafer is microstructured using UV lithography. The resulting structure serves as a mold for creating the chip. The polydimethylsiloxane (PDMS)-cross-linker mix, purchased from Dow Corning (Sylgard 184 Silicone Elastomer), is degassed in a desiccator, after which it is cast onto the mold to from the structures of the microfluidic chip. For this purpose a PDMS/cross-linker ratio of 10:1 is used, followed by curing at 75 °C for 40 mins. To create the PDMS cover of the chip, a PDMS/cross-linker mixture of 20:1 ratio is spin-coated on a glass slide at 2000 rpm for 30 seconds, followed by a curing process over ~15 mins at 75 °C. After punching the inlet and outlet holes, the chip substrate is gently placed onto a glass slide covered with the thin PDMS layer. Finally, the arrangement is cured overnight, leading to PDMS-PDMS bonding.

**3. Experimental procedures**

Prior to an experiment, the oil phase is filled into the main channel using capillary suction, i.e. the oil spontaneously fills the channel since it wets the channel walls very well. By contrast, since PDMS is hydrophobic, the aqueous liquids are introduced into the side channels via syringe pumps (KD Scientific Inc.). The pumps are kept running to build up a pressure head to fix the oil/aqueous interfaces at their desired positions. A high voltage sequencer (LabSmith HVS448) is employed as power supply to provide pulsed and DC voltages. A high-speed camera (Redlake Motion Pro Series Y) is mounted on an inverted microscope (Nikon Eclipse Ti) to capture the behavior and motion of droplets.

# 4. Liquid properties

The liquids used in the experiments were water with different concentrations of NaCl and 1000 cSt silicone oil AP (purchased from Sigma Aldrich). The most important properties of these liquids are listed in the table below. The properties refer to a temperature of 25 °C and atmospheric pressure. The interfacial tension between de-ionized water and silicone oil is ~35 mN/m.

|  |  |  |
| --- | --- | --- |
| Property | De-ionized water | Silicone oil |
| Density [kg·m-3] | 997 | 1090 |
| Dynamic viscosity [10-3 Pa·s] | 0.89 | 1000 |
| Relative dielectric permittivity [-] | 78.4 | 2.5 |

# 5. Determination of the electrostatic force

The electrostatic force on the droplets was determined based on the expression for the viscous drag on a spherical particle. For this purpose, the velocity of a droplet  was determined from the recorded videos, and the electrostatic force was equated with the viscous drag force, i.e.

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where  is the droplet charge,  the electric field strength,  the oil viscosity,  the droplet radius,  the ratio between the oil viscosity and the viscosity of the droplet liquid. The expression for the viscous drag force is that of the Hadamard–Rybczynski equation (Leal, 2007), a generalization of the Stokes drag formula for the case that a spherical droplet or bubble is considered instead of a spherical particle.

# 6. Evolution of the droplet diameter

In Figure 4 the evolution of the droplet diameter during the reciprocating motion over a few hundred cycles is displayed for a voltage of 250 V, showing a rather gradual decrease of the droplet diameter. Independent of the initial droplet diameter, when a critical diameter is reached, a rapid shrinkage of the droplet sets in. This behavior seems to be rather independent of the applied voltage. In Figure S2 corresponding results for a voltage of 300 V shown, for the same salt concentration of 0.17 mM. These data corroborate the findings from the experiments with 250 V, i.e. the existence of a critical droplet diameter independent of the initial diameter.



***Figure S2****. Evolution of the diameter of four different droplets over a large number of cycles. The horizontal line indicates the approximate value of the critical diameter and serves as a guide to the eye. The salt concentration was 0.17 mM and the voltage 300 V.*

**References**

Leal, G. L. (2007). *Advanced Transport Phenomena*. Cambridge University Press, Cambridge.