Supporting information

The measurement of hydrodynamic resistance of microdroplets

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1. Materials and methods.

Fabrication of microfluidic devices.
The chips (the measurement droplet chip) were fabricated in a 5-mm thick polycarbonate plate (Makrolon GP Clear 099, Bayer, Germany) using a CNC milling machine (MSG4025, Ergwind, Poland). Next, the milled plate was thermally bonded to a flat 2- mm thick plate under the pressure (30 min, 130 °C). Then, the chip's surface was modified using fluorosilane (1720 Novec, 3M, USA). After the modifying agent had been introduced to the channel, the whole chip was heated and kept in the temperature of 85°C until the fluid evaporated. The procedure was repeated two twice.

The capillary tubing (Teflon FEP tubing, Dolomite, UK, I.D. 0.25 mm, O.D. 1.6 mm) was placed in the polycarbonate frame (support) in order to place sensors at a known distance from each other. The height and width of the frame corresponded to the outer diameter of the applied tubing. A reference droplet was formed with the use of a simple T-junction made of the same material as the capillary tubing - a 3-mm thick Teflon FEP sheet, which was drilled to fit the capillary.

The inlets of the dispersed phase were connected to resistive steel capillaries (O.D. 400 µm, I.D. 205 µm, length 200 cm, Mifam, Poland) extending from the valves using short segments of Tygon® tubing (~ 2 cm, O.D. 0.91 mm, I.D. 0.25 mm, Ismatec, Switzerland) to connect the capillaries with the needles. In turn, the inlets of oil phase were connected with the use of Teflon FEP tubing (Dolomite, UK, I.D. 0.8 mm, O.D. 1.6 mm) to the valves.

Automation and microfluidics.
Customised software was written in C programming language and was loaded to the microprocessor AT91SAM7S256 (Atmel, USA) as firmware. The microprocessor controlled three valves (V165, equipped with Z070D coils, Sirai, Italy) and four light-to-voltage sensors (TSL257, Taos, USA). The pressure applied to the oil reservoirs was controlled employing manual pressure regulators (Bosch Rexroth PR1-RGP, Germany) and monitored using digital manometers (AZ 82100, AZ Instruments, Taiwan). The generation of droplets was aided with an edge-detection algorithm to track the process of microdroplet formation and control the volume with an accuracy of ~0.1%. The inaccuracy of positioning of detecting sensors on the chips was 5 µm, and the inaccuracy of detecting the edges of droplets was 2 µs.

The liquid flowing out from the chips was weighted onto a balance (Sartorius Cubis MSA2.7S0TRDM ultra micro-balance, Fisher Scientific) in a fixed time interval. After that, the mass was divided by the surface area of the cross section of the reference droplet chip to calculate the average speed of the continuous phase.

Manostat.

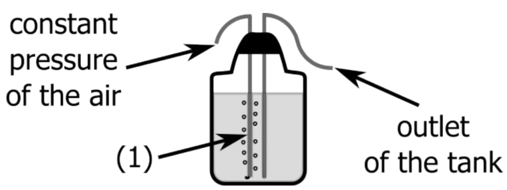

Fig. S1 shows the manostat employed in the experiment. A manostat is a device that maintains constant pressure at the outlet of the tank. In the presented form, the output pressure from the reservoir is constant, while the end of the capillary (1) is below the fluid level.

2. Technical description of the experimental system.

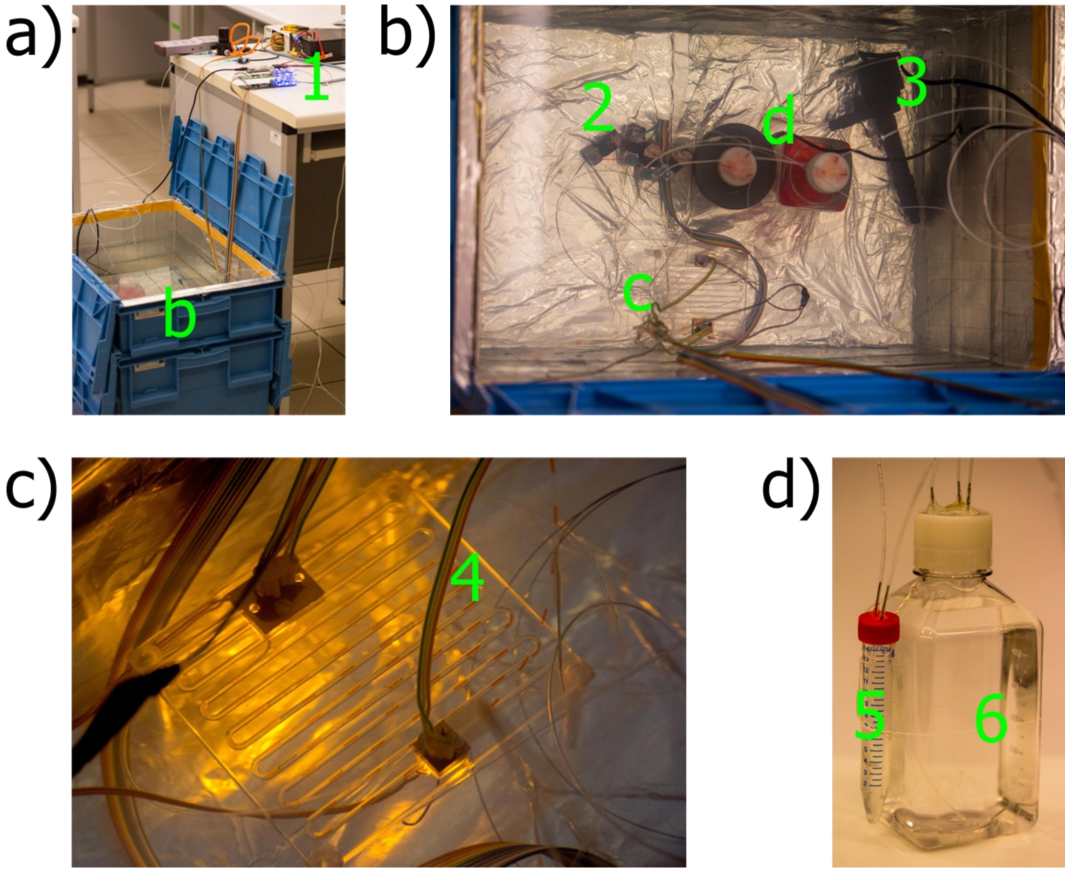

Fig. S2 The photographs of the experimental system. The system consists of:

- the microprocessor AT91SAM7S256 (Fig.S1a-1), which is the main part of the system. Its custom written firmware enables the users to control the bi-stable valves (Z070D, Sirai, Italy) - Fig.S1b-2) - and to detect the droplets.
- 100-liters vessel filled with water used as a thermostat box. The concept is to stabilise the temperature with the use of Peltier modules placed inside the pump (Fig. S1b-3) which forces the circulation of liquid in the vessel. The PID temperature control was programmed into the microprocessor. The system enables to maintain a stable temperature within the accuracy of 0.05^{o}C during 24 hours.
- the detection module (Fig.S1c-4), which is placed on the chips, is used to check i) the appearance of droplets under the sensor, ii) the length (the volume - after calibration) of droplets, and iii) the distance between droplets in a train. The module consists of light-to-voltage converters (TSL257, TAOS), LED diodes, 50-μm apertures (placed: i) between sensors and the surface of a chip, and ii) between led diodes and the surface of the chip), and digital electronics what allowing its generates appropriate triggering signal to the microprocessor. Signal was correlated with the appearance of droplets at the defined place.
- Oil containers (Fig. S1d-6) are pressurised by an outer compressor using a manual pressure regulator. Teflon FEP capillaries transport oil from the tanks to the chips. A microfluidic capacitor (Fig.S1d-5) was applied to establish the flow rate within 0.5 μl/min. The stability of flow rate was checked employing a microbalance.

3. The change of hydrodynamic resistance of a droplet as a function of the length of the droplet and the capillary numbers.

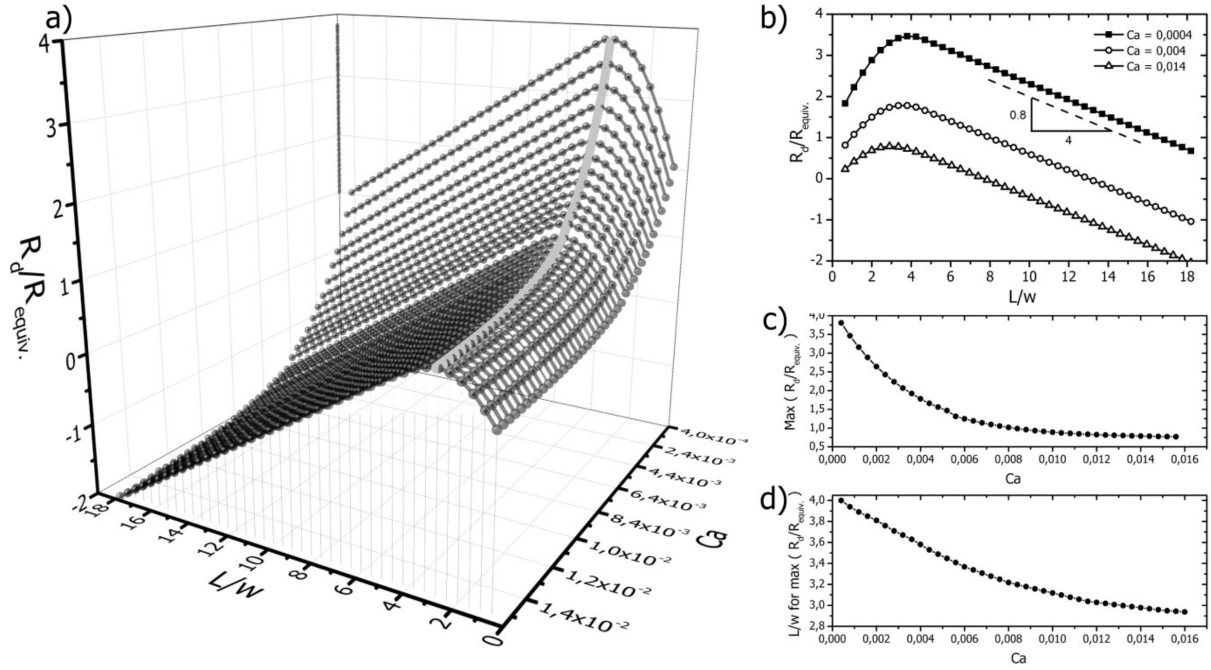

Fig. S3 Graphs illustrate the change of hydrodynamic resistance of droplets flowing in a square ($360\ \mu m\ x\ 360\ \mu m$) cross section channel. a) The 3D graph of the modification of hydrodynamic resistance of the droplet as a function of the length of droplet and the capillary number. $R_{equiv.}$ corresponding to the hydrodynamic resistance of a w-length channel filled with FC-40 calculated from the Hagen-Poiseuille equation. b) The graph of the change of hydrodynamic resistance of a droplet as a function of the length of the droplet for three different capillary numbers. c) The graph shows the change of a maximum of hydrodynamic resistance of the droplet with increasing the capillary number. d) The graph shows the position of a maximum of hydrodynamic resistance of the droplet expressed in a length of the droplet as a function of capillary number. The fixed viscosity ratio of the water phase to the oil phase equals 0,217.