

Microfluidic generation and optical manipulation of ultra-low interfacial tension droplets

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ABSTRACT

We present a microfluidic platform for the generation, characterization and optical manipulation of monodisperse oil droplets in water with equilibrium interfacial tensions on the order of $0.1\text{--}1\mu\text{N/m}$. An oil-in-water emulsion containing the surfactant Aerosol OT, heptane, water and sodium chloride under conditions close to the microemulsion phase transition was used. Through active control of the emulsion salinity and temperature, our microfluidic platform offers the unique capability of tuning the interfacial tension of droplets in the range of $1\mu\text{N/m}$ to few mN/m according to the operation required. Upon collection in a separate observation chamber, droplets were characterized by using video microscopy-based measurement of thermally-induced capillary waves at the droplet interface. Holographic optical tweezers were used to manipulate the droplets and construct 3D nanofluidic networks consisting of several droplets connected by stable oil threads a few nanometers across.

Keywords: Ultra-low interfacial tension, droplet microfluidics, optical tweezers, optofluidics, nanofluidic networks

1. INTRODUCTION

Ultra-low interfacial tension (ULIFT) oil in water droplets support a growing number of exciting applications. As the interfacial tension reaches values as low as $1\mu\text{N/m}$, optical fields¹ can be used to sculpt oil droplets into more complex shapes, possibly leading to new approaches for the synthesis of asymmetric solid particles with user-defined shapes.² Additionally, in the ULIFT regime when a single droplet is separated into two droplets by two optical traps, the two droplets remain connected by a stable thread of oil with a typical diameter of less than a hundred nanometers.³ This phenomenon enables generation of complex nanofluidic networks created and controlled by light.⁴

Microfluidic techniques for generating emulsion droplets offer several advantages with respect to macroscopic emulsification methods, such as high precision control over droplet size and monodispersity, stability, reproducibility and ultra-high throughput.⁵ However, since the droplet formation within microfluidic devices is generally the result of a spontaneous process where the flow viscous stresses are balanced by the interfacial tension at the liquid-liquid interface,⁶ microfluidic methods are more challenging to implement at low and ultra-low interfacial tensions (namely, below 0.1 mN/m). Under these conditions, the interfacial instabilities induced by the capillary forces, which drive break-up processes, are dramatically slowed down. As a consequence of that, the effects of instabilities become negligible on the time scale of thread formation and a stable jet is formed instead.⁷

In recent years, oil-in-water interfaces with ultra-low interfacial tension have been generated within microfluidic devices by adding surfactants in both phases. In order to perturb an otherwise stable jet⁸ and to promote

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droplet formation via the Rayleigh-Plateau instability, the oil-water interface can be destabilised by using a mechanical vibration source.⁹ Alternatively, if the interface formation process is fast enough that surfactant cannot equilibrate at the interface, the dynamic interfacial tension of the newly formed interface is not ultra-low and the jet can spontaneously break up under the Rayleigh-Plateau instability with no need of external perturbation sources. This strategy has been used by Hashimoto et al.¹⁰ to produce ULIFT water droplets in oil within a flow focusing junction device. However, the same Authors showed that once the dynamic interfacial tension reached its equilibrium value, spatial confinement and variation of the channel width (such as expansions and contractions) induced extreme deformation and shear-driven instabilities on droplets, thereby losing any control over the final droplet size distribution. In order to overcome these instabilities, emulsion could be produced at low and moderate surfactant concentrations in the continuous phase, so that the equilibrium interfacial tension would not be ultra-low and droplets would remain stable against shear-induced rupture and coalescence. A surfactant-rich continuous phase could be added to the emulsion in a separate step after formation, thereby reducing the interfacial tension to ultra-low values. However, the resulting monodisperse ULIFT droplets would be very difficult to handle since even low viscous stress, as those induced by nearby walls, would trigger shear-driven instabilities at the droplet interface.¹¹

In this work, we present a microfluidic platform for the generation and the optical manipulation of stable monodisperse oil droplets in water whose final interfacial tension is of the order of $0.1\text{--}1\text{ }\mu\text{N/m}$. Our innovative method relies on a tuneable oil-water formulation whose interfacial tension can be actively controlled within the microfluidic environment. Our platform is capable of producing ULIFT monodisperse droplets with diameters in the range of $5\text{--}30\text{ }\mu\text{m}$ and high stability against coalescence as well as rupture induced by hydrodynamic stresses. We first use our platform to investigate the effects of temperature and salinity on the droplet generation process (Section 4.1). After formation and collection in a separate chamber, the droplet mechanical properties are assessed by measurement of the thermally-driven capillary waves at the droplet interface (Section 4.2). Finally, 3D nanofluidic networks are created by the simultaneous manipulation of monodisperse ULIFT droplets via holographic optical tweezers (Section 4.3). Our microfluidic tool allows for the accurate and repeatable delivery of ULIFT droplets with precise control over composition and size and thus offers the opportunity to improve and extend the field of applications of optical manipulation of ULIFT droplets³ as well as to investigate the fundamental chemistry and physics behind them.

2. METHODS AND MATERIALS

2.1 The oil-water-surfactant system

In our experiments heptane (VWR, 99%) was used as the dispersed phase and an aqueous solution containing NaCl and diethylhexyl sodium sulphosuccinate (AOT) (Sigma-Aldrich, 98%) as the continuous phase. A detailed description of this system is reported elsewhere.^{12–15} For our purposes, it is enough to recall that Aerosol OT has closely matched hydrophilic and lipophilic properties that permit phase transitions in emulsion formation by increasing the hydrophobic character. Either increasing salt concentration or reducing the temperature can reverse the direction of the natural curvature of the surfactant film from oil-in-water to water-in-oil and hence produces an inversion in phase continuity. Such a transition thus corresponds to a sharp decrease of the interfacial tension, which can reach values down to $0.1\text{ }\mu\text{N/m}$, provided the surfactant concentration exceeds the critical micelle concentration (cmc). The temperature corresponding to the minimum attainable interfacial tension for a given salinity is denoted as the phase inversion temperature (PIT). For AOT solutions, the PIT varies from 15°C to 40°C when salt concentration increases from 33mM to 84mM . The relationship between PIT and salinity as well as the dependency of interfacial tension on salt concentration and temperature for the heptane-NaCl-water-AOT system have been characterized by Aveyard et al.^{13–15} through spinning droplet tensiometry.

2.2 Microfluidic chips and image system

Droplets were generated in flow-focusing devices with a cross-junction,¹⁶ fabricated by Dolomite Microfluidics via standard photo-lithography and glass etching techniques. The cross-junction consisted of four channels $135\text{ }\mu\text{m}$ in length which joined at right angles. The cross-junction was connected to $500\text{ }\mu\text{m}$ width inlet and outlet channels via expansion and contractions (see Figure 1b). Droplets with diameters in the range of $9\text{ }\mu\text{m}$ to $30\text{ }\mu\text{m}$ were produced by using $14\text{ }\mu\text{m}$ depth devices with a $17\text{ }\mu\text{m}$ width junction whereas droplets with diameters in the

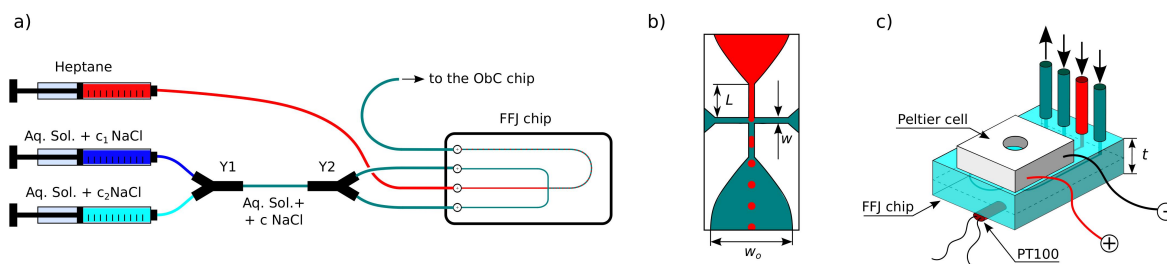


Figure 1. a) Schematic view of the microfluidic platform. b) Schematic of the cross-junction where heptane droplets were formed. The dimensions of the channels are the following: $w_o = 500 \mu\text{m}$, $L = 135 \mu\text{m}$, $w = 8 - 17 \mu\text{m}$. c) Three dimensional schematic view of the on-chip temperature control system used to characterize droplet formation under varying temperature conditions. The channels were located in the middle plane (dashed lines) of the FFJ glass slab, whose total thickness was $t = 4 \text{ mm}$.

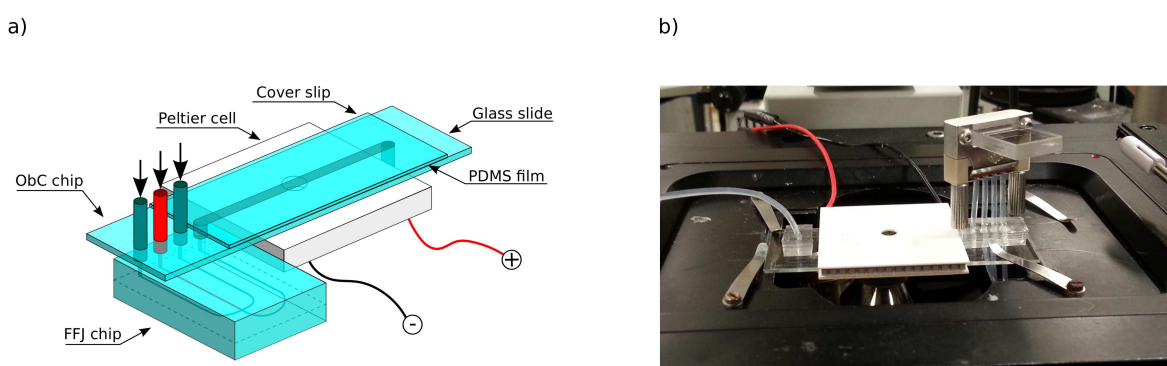


Figure 2. Three dimensional schematic view a) and picture b) of the FFJ and ObC chips assembly. For droplet characterization and optical manipulation purposes, the emulsion temperature was controlled in the ObC chip through Peltier module, whereas droplets were formed in the FFJ chip at room temperature.

range of $5 - 8 \mu\text{m}$ were generated by using $5 \mu\text{m}$ depth devices with $8 \mu\text{m}$ width junctions. Hereafter these droplet formation chips are referred to as the flow focusing junction (FFJ) chips. Syringe pumps (WPI-Aladdin2-220) were used to supply the dispersed phase in the central channel and the continuous phase in the side channels. Measurements were performed at least five minutes after changing the flow rates of the two phases to ensure the system stability.

After formation, droplets were transferred into a separate device designed and fabricated for droplet storage, characterization and manipulation purposes (see Figure 2). The device was made of one microscope glass slide and a cover slip separated by a $30 \mu\text{m}$ thickness PDMS layer, the fabrication protocol being reported elsewhere.¹⁷ We refer to that device as the observation chamber (ObC) chip. Two different configurations of the microfluidic platform were realised. In the first configuration (Figure 1c), suitable for the characterization of the droplet formation regimes, the FFJ chip was fitted with on-chip temperature control, consisting of a resistance thermometer (PT100 Class A) and a Peltier cell (Ferrotec) attached to the bottom and top external walls of the chip, respectively. The Peltier cell had a central 5 mm diameter hole to allow optical access to the cross-junction. The cell was driven by a proportional-integral-derivative (PID) control unit (Electron Dynamics Ltd.), which allowed for temperature control with a precision of 0.1°C . To allow the system to reach thermal equilibrium, measurements began at least three minutes after the chip temperature had been set to a new value. In the second configuration of the platform, suitable for droplet characterization and optical manipulation, the Peltier module was removed from the FFJ chip so that droplets were generated at room temperature. A Peltier cell with a central hole to allow optical access was attached to the top wall of ObC chip in order to adjust the emulsion temperature during droplet characterization and manipulation experiments.

Images of droplets within both the FFJ and ObC chips were captured with an Olympus IX81 inverted

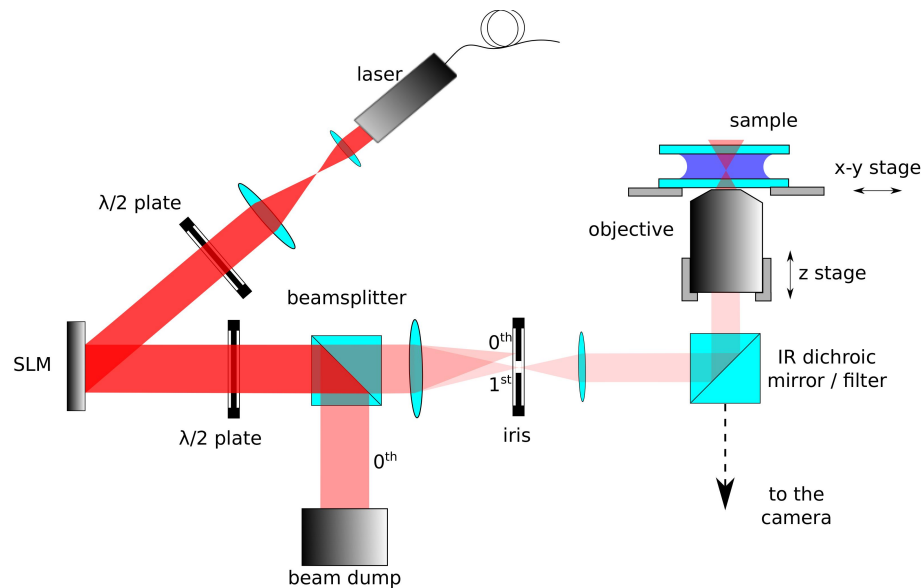


Figure 3. Schematic view of the holographic optical tweezers. The laser wavefront was modulated by the SLM to scan the beam in quick succession between the required trap positions. Only the light of the first diffraction order could reach the sample, the zeroth and higher orders being stopped by the beam dump and the iris diaphragm.

microscope fitted with a CCD camera (Q-Imaging Retiga EXi fast). Image post-processing for droplet sizing and characterization was performed with custom Java macros implemented in ImageJ and with Python code.

2.3 The optical trapping system

A holographic optical tweezers system was used to manipulate ULIFT droplets and create nanofluidic networks. The linearly polarized beam from a Ytterbium fiber laser source (20W at 1070nm) was first expanded using two IR doublets to 20 mm diameter in order to fill the (1280x1024 pixel) display of a ferroelectric liquid crystal on silicon (FLCOS) spatial light modulator (SLM) (ForthDD SXGA-R-H1). A second pair of IR doublets was used to adjust the beam waist in order to slightly overfill the back-aperture of 60x 1.4 N.A. oil objective mounted on a Nikon TE2000-U inverted microscope. A Nikon cube fitted with a IR dichroic mirror and a IR filter was inserted in the microscope carousel to direct the trapping beam towards the objective while preventing any beam reflection from reaching the CCD camera (ORCA-ER Hamamatsu). To maximise the intensity of the first diffraction order as well as to dump the unmodulated (zero-th order) beam, two half-wave plates were placed before and after the SLM, followed by a polarizing beamsplitter which directed most of the zero-th order beam into a purpose built commercial beam-dump. The unmodulated portion of the beam is particularly detrimental for ULIFT droplet manipulation purposes as it would cause significant heating of the sample and would induce temperature gradient within the sample, thereby compromising the droplet stability. The optical train after the SLM was thus aligned with respect to the +1 diffraction order and the portion of zero-th order beam which was transmitted through the beamsplitter as well as the -1 diffraction order were fully stopped by using an iris diaphragm, placed at the beam waist between the two IR doublets.

A time multiplexed approach was used simultaneously to manipulate several droplets through multiple independently steerable traps. The 24 bit color planes of the SLM were used to display for an equal length of time a sequence of simple binary holograms in quick succession to scan the beam between the required trap positions. This approach allows for the generation of a maximum of 24 independent traps. The calculation of the binary holograms was performed through a graphic card (NVIDIA GeForce 8600GT 512MB RAM GPU) and OpenGL Shading Language (GLSL) code. A Labview (National Instruments Corp) graphical user interface was used to allow fast and easy control over the trap generation and motion as well as image acquisition processes. A more detailed description of this holographic optical tweezers setup and its performances can be found elsewhere.¹⁸

3. THE MICROFLUIDIC PLATFORM

The heptane-water emulsion containing AOT and NaCl reaches the ULIFT regime when the system is very close to the microemulsion phase transition. Such a condition can be obtained by finely tuning the salinity level and the temperature of the emulsion. We thus devised a microfluidic system where both those parameters could be controlled. The final salinity of the continuous phase was obtained by mixing two aqueous solutions with different salt concentrations. Two syringes (see Figure 1a) were charged with c_1 and c_2 mM NaCl aqueous solutions plus 2mM AOT. The liquids from the two syringes joined together in a Y junction (Y1) and fully mixed by flowing in a 250 μm diameter FEP tubing. Denoting the flow rates in the two syringes as Q_{c1} and Q_{c2} , the final salt concentration of the mixed phase can be expressed as

$$c = \frac{c_1 Q_{c1} + c_2 Q_{c2}}{Q_{c1} + Q_{c2}} \quad (1)$$

After mixing, the flow split at the junction Y2 and entered the side channels of the FFJ chip. Assuming a relative error of $\delta c_i/c_i = 0.2\%$ (for $i=1,2$) for the salinity of the aqueous solutions and $\delta Q_{ci}/Q_{ci} = 1\%$ (for $i = 1, 2$) for the flow rates of the syringe pumps, we can estimate that the accuracy on the salt concentration of the mixed phase is about $\delta c/c = 0.3\%$. For a 50mM NaCl aqueous solution, that means an approximate error of 0.2 mM in the final salt concentration.

To characterize the effects of temperature on droplet formation, the FFJ chip temperature was controlled through a thermal control unit. The Peltier Cell size and heat pumping capacity were chosen so that at the cross-junction the flowing liquids have already reached the thermal equilibrium. The effects of the central hole of the Peltier module were assessed through finite element analysis in COMSOL Multiphysics (COMSOL Ltd.). Numerical simulations showed that with a typical room temperature of 23°C and for an average chip temperature of 30°C the standard deviation of the temperature field in the volume of the FFJ glass slab under by the Peltier unit is about 0.2°C. That value can be considered as a good estimate for the precision of the emulsion temperature measurements. A similar thermal control unit was also installed on the ObC chip (see Figure 2), where droplet characterization and optical manipulation were performed. The mechanical characterization of the ULIFT droplets was performed with an air-immersion long-working distance 60x objective (N.A. 0.7), which allowed us to measure the emulsion temperature through a resistance thermometer attached to the bottom wall of the chip. However, optical manipulation has to be carried out with liquid immersion high numerical aperture (low working distance) objectives. Because of space constraints, the temperature sensor could no longer be placed near the working volume of the ObC chip so temperature readings were not available at the time of droplet optical manipulation. However, the Peltier cell voltage was manually adjusted in order to achieve the highest droplet deformability.

4. RESULTS AND DISCUSSION

Droplets cannot readily be generated in the ULIFT regime because the effects of capillary forces, which drive the interfacial instability leading to the breakup of the dispersed phase stream, are dramatically slowed down. Consequently, for interfacial tension lower than a critical value γ_c ¹⁹ droplets do not form at the cross-junction and parallel flows of the two phases are obtained instead. If, however, the time scale for interface generation is less than the characteristic diffusion time for the surfactant to the interface, the equilibrium surface coverage is not reached on the time scale of droplet formation.²⁰ Under these conditions, the dynamic interfacial tension γ_d assumes values between the interfacial tension at equilibrium γ_e and the interfacial tension of a clean surfactant-free interface γ_0 , depending on the device geometry, the flow rates and the type and concentration of surfactant.²⁰ For γ_d typically higher than γ_c , it is hence possible to produce monodisperse droplets immediately at the junction whereas the droplet equilibrium interfacial tension still lies in the ULIFT regime. For typical surfactant concentrations in the millimolar range, the diffusion timescale is of the order of milliseconds. After formation, the droplets go through the junction and enter the wider output channel, where the diffusive and convective transport of surfactant molecules to the interface²⁰ causes the interfacial tension γ_d to drop to ultra-low values on a time scale of tens of milliseconds after generation. For that reason, ULIFT droplets are unstable and they can easily tear apart due to the high viscous stresses downstream of the junction, yielding highly polydisperse emulsions.¹⁰

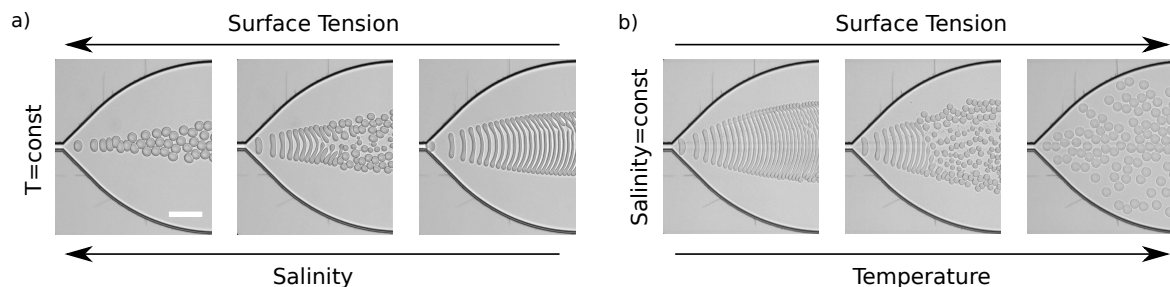


Figure 4. Upon formation, droplets entered the expanding output channel and were subjected to viscous stresses causing them to deform. Droplet deformability was investigated at varying salinity levels and constant temperature (a) as well as at varying temperatures and constant salt concentration (b). The white scale bar is $100\ \mu\text{m}$.

The most effective method to produce and manipulate monodisperse ULIFT droplets is to control the equilibrium interfacial tension according to the operation required. For droplet generation and transport, γ_e has to be higher than γ_c and the capillary number Ca lower than a critical value Ca_c whereas for droplet storage, manipulation and optical deformation γ_e can be lowered down to the ULIFT regime. Such control is quite difficult to implement when γ_e mainly depends on the concentration of surfactant in either phases, as it occurs for the oil-water-surfactant systems typically used in droplet microfluidics. On the contrary, for the heptane-brine-AOT system at a surfactant concentration higher than the cmc, γ_e strongly depends on salinity and temperature. By controlling these two parameters, the equilibrium interfacial tension can be independently tuned in the FFJ chip for droplet generation and in the ObC chip for droplet storage, characterization and manipulation.

4.1 Effects of salinity and temperature on droplet formation

We first assess the effects of salinity on droplet formation by fixing the FFJ chip temperature and varying the emulsion salinity in the range corresponding to the lowest interfacial tensions. The continuous phase syringes were filled with aqueous solution at salt concentrations $c_1 = 0\ \text{mM}$ and $c_2 = 100\ \text{mM}$. The corresponding flow rates Q_{c1} and Q_{c2} were varied in order to tune the final salinity of the emulsion. The total water flow rate $Q_c = Q_{c1} + Q_{c2}$ and oil flow rate Q_d were fixed to $0.2\ \mu\text{L}/\text{min}$ and $0.05\ \mu\text{L}/\text{min}$, respectively. Figure 4a shows the generated droplets flowing outside of the junction for salinity levels between $50\ \text{mM}$ and $100\ \text{mM}$ for a fixed chip temperature of 26.2°C . Interpolating the data available in the literature,¹³ the interfacial tension of the heptane-water-AOT-NaCl system at 26.2°C and $50\ \text{mM}$ NaCl is expected to be around $0.3\ \mu\text{N}/\text{m}$. Close to these conditions, γ_e depends strongly on the concentration of NaCl with higher salinity level corresponding to higher interfacial tensions. The interfacial tension can be qualitatively assessed through the deformations droplets underwent in the expanding output channel. Indeed, as droplets left the junction, the viscous stresses exerted by the continuous phase flow in the expanding output channel deformed the droplets.

Even though the geometry of our droplet generation device does not allow us to easily estimate the character and the intensity of the viscous stresses, our experimental data showed that for the examined flow rates droplets did not break up in the output channel when the equilibrium interfacial tension was higher than $0.1\ \text{mN}/\text{m}$. Moreover, at constant temperature (hence, constant liquid viscosity) and constant liquid flow rates, the viscous stresses are expected to be the same for all experiments. Consequently, the capillary number Ca was a function of the interfacial tension only and the deformed shape of the droplets exclusively depended on the interfacial tension of the oil-water interface with higher deformations corresponding to lower values of γ_e . At high salinity level, droplets were only slightly deformed by the viscous stresses and proved stable against rupture (Figure 4a, left image). However, if the capillary number exceeds a critical value Ca_c , no equilibrium droplet shape exists in order to balance the viscous and capillary forces and the flow keeps deforming the droplets until Rayleigh-Plateau instabilities prevails and droplet breakup occurs. Such a condition occurred when salt concentration, and thus interfacial tension, was reduced below a certain threshold (Figure 4a, central image). For salt concentrations very close to the value corresponding to the phase inversion (namely, $\sim 51\ \text{mM}$ at $\sim 26.3^\circ\text{C}$), the droplets remained stable to break up within the field of view of the microscope (Figure 4a, right image). Such a result can be explained by comparing the breakup time and the drop residence time in the field of view. We can assume that

in supercritical condition ($Ca > Ca_c$), the time of capillary breakup scales with the visco-capillary time $t_{vc} = \frac{\eta_c d_0}{\gamma_e}$, where η_c is the dynamic viscosity of the continuous phase, d_0 is the undeformed droplet radius. Under the same condition of temperature and flow rates, lower interfacial tensions would hence result in longer breakup times. For extremely low interfacial tensions ($\sim 1 \mu\text{N/m}$), the breakup time can exceed the residence time and droplets no longer break up within the field of view of the microscope.

For a given salinity the equilibrium interfacial tension can still be modified through the temperature. Therefore we have also investigated droplet generation at varying temperatures for a fixed salt concentration. First, the system was brought very close to the microemulsion phase transition (Figure 4b left image) and then the temperature was gradually increased from 26°C to 80°C while keeping the salt concentration at 50mM. As for the previous experiments, the total flow rate of the continuous phase was $Q_c = 0.2 \mu\text{L/min}$ whereas the flow rate of the dispersed phase was $Q_d = 0.05 \mu\text{L/min}$. Under those conditions, the droplet interfacial tension is expected to increase with the temperature. In agreement with this prediction, the experimental results show that for a high value of γ_e , the capillary force successfully opposed the viscous stresses, thereby preventing droplet rupture in the outlet channel (Figure 4b right image). The resulting droplet population was monodisperse. It is worth noting that the increase in temperature does not only affect the interfacial property of the emulsion, but it also changes the bulk rheology of the liquid phases. Indeed the viscosity of heptane and water decrease by about 19% and 35%, respectively, for a temperature rise from 20°C to 40°C . The viscosity affects the fluid stresses as well as the droplet size, so it is not possible to relate the droplet shape directly to the interfacial tension as in the previous experiments.

Our experiments show that droplet deformability depends on water salinity and temperature and it increases with decreasing γ_e . Such behaviour demonstrates the capability of the microfluidic platform to tune the equilibrium interfacial tension of the oil-water interface by controlling both salt concentration in the continuous phase and the emulsion temperature. Such fine tuning allows us to suppress shear-driven and Rayleigh-Plateau instabilities and obtain monodisperse droplet populations. The typical droplet diameter is in the range from $11 \mu\text{m}$ to $30 \mu\text{m}$ when $14 \mu\text{m}$ depth FFJ chips were used. Droplet diameters can be reduced down to $5 \mu\text{m}$ by using $5 \mu\text{m}$ depth FFJ chips.

4.2 ULIFT droplet characterization: thermal capillary waves at the droplet interface

It is well known that thermal motion is able to produce statistical fluctuations of the position of a two-phase interface.²¹ The typical amplitude of those thermally-induced capillary waves scales as $\sqrt{k_B T / \gamma}$, where k_B is the Boltzmann constant and T the absolute temperature. For the most common water-oil-surfactant systems adopted in droplet microfluidics, the interfacial tension is of the order of 1 to 10 mN/m, which sets the wave amplitude in the range of 1nm. Such a small perturbation can only be detected via light and x-ray scattering techniques and, hence, the interface of a droplet appears to be smooth down to the molecular length scale. On the other hand, if the interfacial tension is lowered down to $0.1\text{--}1 \mu\text{N/m}$, the interface roughness increases up to 50-200 nm, and the thermal capillary waves can be observed using standard optical microscopy.²²

We thus monitored the thermally-driven perturbations at the droplet interface to characterize the droplet behaviour at different salinity and temperature conditions as well as to verify that the droplets can effectively enter the ULIFT regime. Droplets were generated at lab temperature with high salinity levels in order to satisfy the condition $\gamma_e > \gamma_c$. After formation, the monodisperse droplets were transferred to the ObC chip. The syringe pumps were then stopped and the ObC and FFJ chips were isolated from the syringes and the waste reservoir by means of shut-off valves. The droplet finally rested in a quiescent continuous phase at the top wall of the observation chamber, whose temperature was adjusted through the thermal control unit (Figure 2). As the emulsion temperature was increased towards the PIT, the droplet interfaces, initially rigid, began to fluctuate under the effect of thermal motion.

The droplet interface position was detected via image processing analysis implemented in Python. Briefly, starting off an initial guess for the droplet centre, the inflection point r_i of the radial pixel intensity $I_i(r)$, averaged over the azimuthal angles from θ_i to $\theta_i + \Delta\theta$, was determined with subpixel precision. That operation was repeated for equally spaced azimuthal angles θ_i varying between 0 and $(N - 1)\Delta\theta$, where $N = 2\pi/\Delta\theta$. The detected interface points, whose polar coordinates are (θ_i, r_i) , were then fitted to a circle. The centre of the best fitting circle was then used as new origin of the polar coordinate system and the radial pixel intensities $I_i(r)$

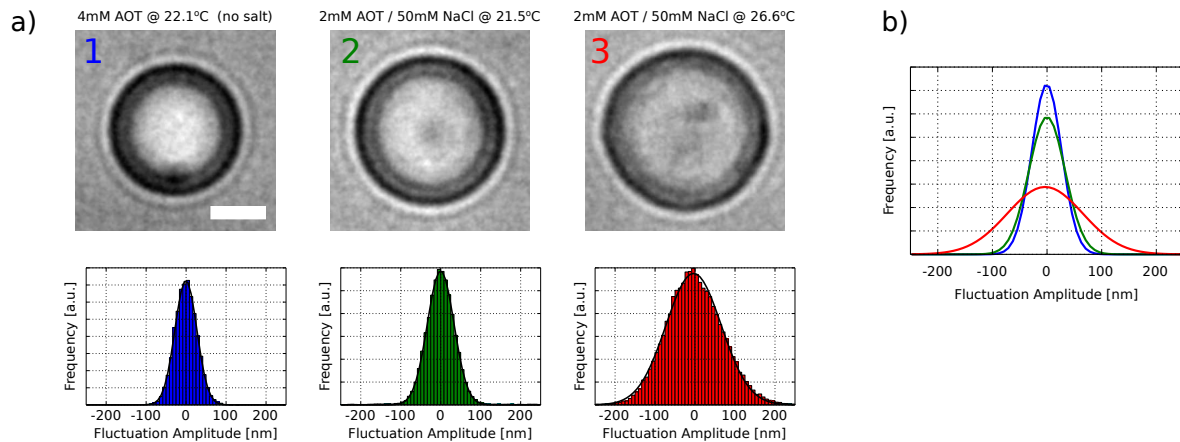


Figure 5. The interface fluctuations of droplet interface were analysed in three different conditions (cases 1,2,3). a) Micrographs of droplets resting in the ObC chip (top images) and the corresponding normalized histograms of the interface fluctuation amplitudes (bottom images). Droplet diameters are $11.82\ \mu\text{m}$ (case 1), $13.26\ \mu\text{m}$ (case 2) and $14.9\ \mu\text{m}$ (case 3). b) Comparison between the best-fitting Gaussian curves of the fluctuation amplitude normalised histograms for all three cases. The standard deviations are 27 nm (case 1), 33 nm (case 2), 70 nm (case 3).

as well as the inflection points r_i were calculated again with respect to this new center. Such an operation is required to avoid artefacts due to slight displacement of the droplet between two consecutive frames. The centre of the best fitting circle of one frame is used as an initial guess of droplet center in the consecutive frame. The interface fluctuation amplitude at the angle θ_i was defined as $u_i = r_i - \langle r_i \rangle$, where $\langle . \rangle$ denotes the average over all the analysed frames. The images of the droplets were captured with a 60x (0.7 N.A.) objective and CCD camera (Q-Imaging Retiga EXi Fast1394) at a frame rate of 1Hz, the scale factor and exposure time being $0.109\ \mu\text{m}/\text{pixel}$ and 0.01ms, respectively. At least 200 frames were processed for each droplet interface analysis measurement.

Figure 5a shows the histograms of the fluctuation amplitudes for three different cases. First, a heptane droplet in 4mM AOT water solution with no salt was considered (case 1). Under those conditions, the droplet interfacial tension is expected to be of the order of few mN/m and the interface fluctuation amplitudes cannot be detected due to the limited spatial resolution of the optical system. As a consequence of that, we can consider the standard deviation of the best-fitting Gaussian curve of the corresponding fluctuation amplitude histogram (namely, 27 nm) as a good estimate for the accuracy of the droplet interface tracking method. In case 2, a heptane droplet in 2mM AOT and 50mM NaCl water solution at 21.5°C was examined. According to the literature,¹³ the droplet interfacial tension is expected to be approximately $\gamma_e = 4.5\ \mu\text{N}/\text{m}$. The Gaussian curve fitting to the amplitude histogram resulted in a standard deviation of 33nm, which is of the same order of the interface tracking accuracy. Finally, the chip temperature was adjusted to bring the heptane droplet close to the microemulsion phase transition (2mM AOT, 50mM NaCl at 26.6°C). Under these conditions (case 3), the expected interfacial tension is about $0.5\ \mu\text{N}/\text{m}$ and the measured standard deviation of the fluctuation amplitude was 70 nm, i.e. twice the value for a rigid droplet (case 1). Figure 5b shows the comparison between best-fitting Gaussian curves for the three cases and thus demonstrates that the adopted bright-field interface tracking method is accurate enough to individuate droplets whose interfacial tension is lower than $1\ \mu\text{N}/\text{m}$. To conclude, it is worth noting that the decreasing of interfacial tension from case 1 to case 3 can also be qualitatively assessed through the droplet diameter at the equatorial plane. Indeed, as the interfacial tension decreases, the droplets deform under the effect of buoyancy and they are squeezed against the top wall of the chamber. Smaller interfacial tensions correspond to larger deformations and thus larger diameters at the equatorial plane with this behaviour confirmed by our experimental data.

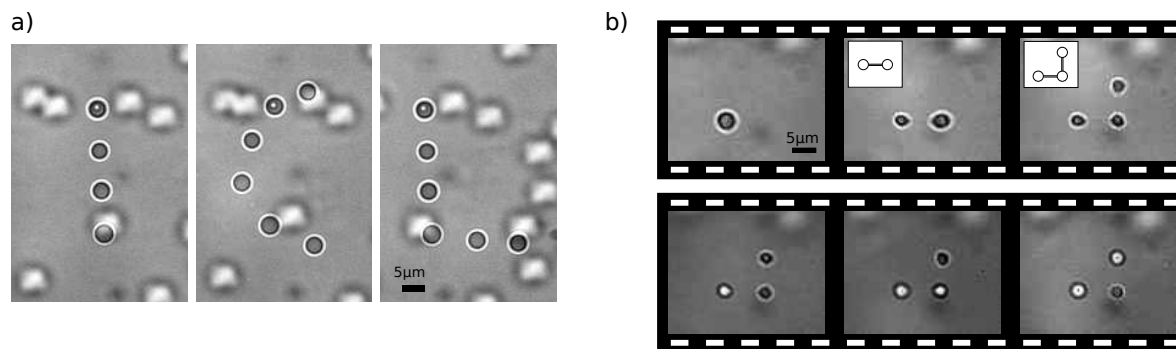


Figure 6. a) Monodisperse rigid droplets are manipulated by using holographic optical tweezers. Six droplets can be arranged so that they show the acronym ICL (Imperial College London). b) Selection of frames which show the formation and the manipulation of a three-dimensional nanofluidic network. The insets display a schematic of the networks to highlight the position of the oil threads connecting the droplets. Those threads are invisible to the microscope in bright-field mode because of their nanometer size.

4.3 Optical manipulation of ULIFT droplets

Our microfluidic platform was finally used to optically manipulate ULIFT droplets as well as create arbitrary three-dimensional nanofluidic networks. Monodisperse droplets 5 μm in diameter were generated by supplying a 5 μm depth FFJ chip with heptane and aqueous solution phases at flow rates of 7 μL/min and 0.05 μL/min, respectively. As in the previous experiments, droplets were produced at room temperature and high salt concentration (namely, 56 mM NaCl) so that a monodisperse population was obtained. Once at rest in the ObC chip, the droplets were manipulated by using a holographic trapping system. Figure 6a shows six rigid droplets being moved away from the channel top wall and arranged so to reproduce the acronym ICL. In the same figure, out-of-focus droplets which were not trapped and rested at the top wall of the chamber can also be seen. Those droplets were manipulated at room temperature (approximately 22°C) and, hence, were rigid.

Adjusting the voltage of the Peltier cell attached to the ObC chip, droplets approached the conditions of microemulsion phase transition, thereby becoming highly deformable. Once the ULIFT regime was achieved, optical traps were used to create arbitrary three-dimensional nanofluidic networks. Figure 6b, which contains a selection of frames extracted from a video, shows the formation and the manipulation of one of those networks. A single droplet was split into two and, subsequently, three droplets connected by nanofluidic threads, whose diameter is predicted to be in the range from 10 nm to 100 nm.⁴ Such a scale length is well below the diffraction limited resolution of the microscope and, hence, the nanofluidic threads cannot be visualized in bright-field mode. However their existence is proved by the recoil force they exert, which causes the deformation of the droplets at the thread connection points as well as the recoil of the droplets when those are released from the trap. After the networks were formed, holographic optical tweezers allowed for independent three-dimensional motion of each droplet. As an example, in Figure 6b it is shown how each droplet could be individually moved out of the objective focal plane.

5. CONCLUSIONS

In this paper we present a microfluidic platform for the generation, characterization and optical manipulation of monodisperse ULIFT oil droplets in water. The device allowed us to tune the interfacial tension of the liquid-liquid interface by accurate control of the salinity and temperature allowing droplets to be generated with common microfluidic techniques, such as the use of a flow-focusing device, with no need of external perturbation sources. The aqueous phase was pumped from two syringes filled with solutions having different salt concentrations. The flow rate ratio of the syringes determined the final salinity of the emulsion. On-chip temperature control units were adopted to adjust the emulsion temperature.

Droplet formation in microfluidic devices is challenging when the interfacial tension is in the ULIFT regime. The growths of interfacial disturbances, which drive the capillary breakup, are extremely delayed and the dispersed phase can form long and stable jets. We showed that droplets can be generated even for equilibrium interfacial tensions in the ULIFT regime, but only if the production rate is fast enough that surfactant cannot equilibrate at the interface. However, after formation the dynamic interfacial tensions quickly drop to ultra-low values and the resulting capillary forces cannot compete against the viscous stresses; the droplets tear apart and the resulting emulsion is polydisperse. To suppress those instabilities and obtain a monodisperse population, the droplet formation was performed at room temperature and high salinity concentrations so that the interfacial tension was higher than the critical threshold $\gamma_c \simeq 0.1\text{mN/m}$.¹⁹ Under these conditions, droplets were highly stable with respect to rupture as well as coalescence.

After formation, droplets were transferred in a separate chip for storage, characterization and manipulation purpose. We proved that droplets finally entered the ULIFT regime by analysing the thermally-induced capillary waves at the droplet interface. Measurement of capillary-waves was performed through bright-field microscopy. The interface detection method for the measurement of interface fluctuation amplitude proved to be accurate enough to discriminate between rigid and soft droplets. Finally, holographic optical tweezers were used to simultaneously manipulate several droplets and to create arbitrary three-dimensional nanofluidic networks.

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