R&D NOTES

Simultaneous Formation of Many Droplets in a Single Microfluidic Droplet Formation Unit

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Introduction

Narrowly dispersed emulsions with droplet size of 0.1–100 μm are of great importance in both science and industry. However, conventional emulsification techniques yield wide droplet size distributions with typical coefficient of variation (CV) of around 40%.[1] Next, most of the energy put into the product is dissipated as heat.[2]

Recently, several new energy-efficient droplet formation systems have been developed, which give more monodisperse emulsions. Highly monodisperse droplets can be produced by single-drop technologies such as flow-focusing devices,[3,4] coflowing systems,[5] T-, Y-, or cross-junctions,[6–8] and microchannels.[9–11] Some of these techniques produce droplets in the desired range; however, the volumetric productivity of one unit is considered too low to be of practical relevance for larger scale applications.

To realize a higher volumetric production rate, it is essential to upscale these systems. In the single-drop technologies, the droplets are formed sequentially, which requires mass parallelization of the droplet formation units (DFU). In shear-based systems such as flow-focusing, coflowing devices, and T- and Y-junctions, both the to-be-dispersed and continuous phase flows need to be precisely controlled at each DFU as the flow rates have a huge influence on the droplet size. Consequently, a parallelized shear-based droplet generator is complex, because it involves not only more units but also the control of the flows in all units. Nisisako and Torii[12] succeeded in mass production of monodisperse droplets of around 100 μm with CV of 1.3% using large-scale microfluidic integration on a chip (256 droplet formation units). Although it is in principle possible to parallelize smaller channels, therewith leading to mass production of much smaller droplets, the difficulties with control of the flows are expected to increase exponentially as the characteristic size of the system decreases and are expected to be far from trivial.

In microchannel (MC) systems as studied by Kawakatsu et al.,[9] Sugiura et al.,[13] Kobayashi et al.,[10] and our group,[11] only the flow of the to-be-dispersed phase needs to be controlled. The continuous flow rate is not a parameter that plays a role in droplet generation, because droplet formation is induced by Laplace pressure differences, and is often referred to as spontaneous droplet formation. A low flow rate is only applied for droplet removal from the DFU, because otherwise it would be blocked by the droplets. These systems seem to be more suitable for scale up; especially, the straight-through microchannel devices of Kobayashi et al. look promising. Monodisperse emulsions with droplet diameters of 4.4–9.8 μm with CV from 5.5% to 2.7% were successfully produced using straight through MC plates with different channel dimensions.[14] Unfortunately, the channel efficiency, which is the percentage of droplet producing channels, was <1% for the plate with the smallest microchannels and only up to 12.3% for the larger ones. This is most probably due to pressure gradients in the system, as was extensively discussed by Gijsbertsen-Abrahamse et al.[15] for emulsification with microsieves, which resemble

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the devices of Kobayashi et al. Next, fabrication inaccuracies could also cause low channel efficiency as mentioned by Kobayashi et al.

In the microchannels discussed in the previous section, droplets are generated one at the time from a so-called terrace that practically empties to form the droplet. In this article, we present a new droplet formation unit, EDGE (edge-based droplet generation), in which a multidroplet formation mechanism occurs that generates many narrowly dispersed droplets simultaneously from the same droplet formation unit. Contrary to the microchannels, where the volume of the droplets is roughly in the same order of magnitude as the volume of the terrace from which they are spontaneously generated, the volume of the droplets formed in this new device is only a small fraction of the volume of oil present on the so-called plateau.

Experimental

The structures and channels were etched with the Deep Reactive Ion Etching (DRIE) technique (Micronit Microfluidics, The Netherlands) in a silicon microchip of 1.5 cm × 1.5 cm. A glass plate was bonded on top of the chip to close the channels. Hydrophilic surfaces needed for oil-in-water emulsion production were created in this way. The unit consists of an oil supply channel of 100-μm wide and 200-μm deep and a continuous phase supply channel with similar dimensions. In between those channels, there is a plateau with fixed width ($W_p = 500$ μm) and length ($L_p = 200$ μm). The plateaus that were used have either of two depths (H_p): 2.6 or 1.2 μm; the plateau being the actual the droplet formation unit in this EDGE system. We define both systems as EDGE-1.2 and EDGE-2.6, respectively, (see Figure 1 for an image of the lay out and the dimensions).

The oil, in our case hexadecane (viscosity $\eta = 3.34$ mPa s), is guided to the plateau via the oil channel. We use a digital pressure controller (Bronkhorst, The Netherlands) to set and control the applied pressure. The pressure needed for hexadecane to flow onto the plateau is determined by Laplace's law:

$$\Delta P = \sigma \cos\theta \left(\frac{1}{R_1} + \frac{1}{R_2}\right) \approx \frac{\sigma}{R_1} \qquad (1)$$

where σ is the interfacial tension, R_1 and R_2 are the radii of curvature of the oil-water interface, and θ is the contact angle. For simplicity reasons, we assume a contact angle of 0°, and as curvature R_2 is very large compared with R_1, the minimal pressure needed here is determined by the smallest curvature, as shown in the right part of Eq. 1. If the pressure exceeds this value, the oil flows on the plateau and droplets will be formed at the edge, where the droplets "fall over the edge" into the channel with MilliQ ultra pure water with 1% SDS as surfactant, which is supplied to the channel with a syringe pump. Typical flow rates for the continuous phase are 300–1000 μl/h.

The emulsification process is visualized using a high-speed camera connected to a microscope. In Figure 1, a snapshot from a movie of a typical experiment with an EDGE-2.6 μm system is depicted; the view is straight from top, and the depth of the various structures is indicated in the image. In the top left corner, an enlarged image of a forming droplet is shown.

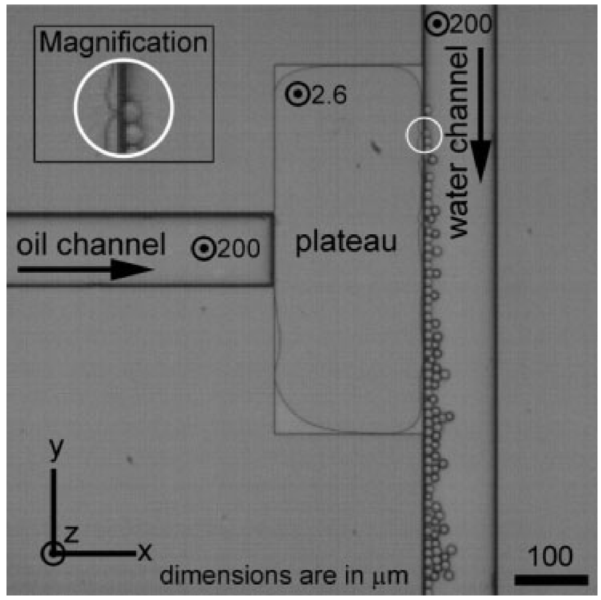

Figure 1. Topview of EDGE unit. From left oil is led through the oil channel to the plateau and into the water channel after droplet formation at the edge of the plateau.

A magnification of droplet formation is shown in the top left corner. Typical dimensions of the structure are indicated in the image.

Droplet formation at the edge of the plateau occurs seemingly at random along the width of the DFU, and at many locations simultaneously, albeit that the corners of the plateau are not used due to Laplace pressure differences. In an EDGE system, similar-sized hexadecane droplets can typically be formed at frequencies of >1500 and >2000 Hz per DFU, for EDGE-2.6 and EDGE-1.2, respectively.

Results and Discussion

The droplet sizes of emulsions produced with both EDGE systems are analyzed through image analysis and with the Mastersizer 2000 (Malvern Instruments Ltd., United Kingdom). The resulting size distributions are depicted in Figure 2, together with an insert of a photo of an emulsion produced with EDGE-1.2. When using image analysis, we find an average droplet size of 7.1 μm for EDGE-1.2, and 14.6 μm for EDGE-2.6 with a CV of ~5% for both EDGE systems; and these CVs are very comparable with values reported in literature, e.g., in the work of Kobayashi et al., who also used image analysis. When determined by Mastersizer, the volume weighted average for EDGE-1.2 is 7.20 μm with a CV of ~10%; for EDGE-2.6, the size is 15.55 μm with a CV of ~16%. There seems to be a systematic difference between both techniques and that may quite well be a result of the limited number of droplets that necessarily can be analyzed by image analysis. Despite the different values, the produced emulsions have a narrow

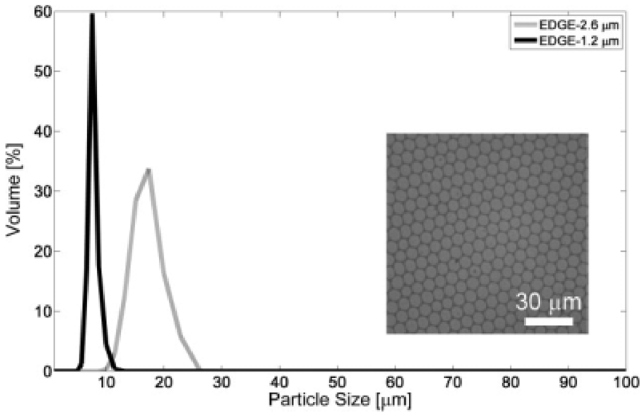

Figure 2. Size distribution of emulsions produced with EDGE-1.2 and EDGE-2.6, together with a micrograph of an emulsion produced with the 1.2 device.

distribution, especially when compared with emulsions made by homogenization.

To study the droplet formation process in more detail, sequential close-up images of a single droplet were made. Figure 3 shows the typical shape of the interface during droplet formation. Please note that we look straight from the top and we can only see one plane; the x–y plane. The droplet becomes visible in image b and grows in time, until the neck with which it is connected to the plateau breaks (image g), and the interface retreats to be filled again (image a).

Growth of the droplet results in a lower Laplace pressure in the droplet according to Eq. 1 with both radii of curvature equal to droplet radius R_d. The droplet in Figure 3b–f is still connected to the plateau through a neck. Very close to the edge of the plateau, it can be assumed that the local pressure in the neck will be approximately equal to the Laplace pressure in the droplet. And this implies that Laplace pressure due to the two curvatures of the neck has to be in accordance with that of the droplet. The curvatures can be found on the plateau, one of them (x-z plane) is fixed at a value of half the height of the plateau (R_{p1}). The curvature in the x-y plane (R_{p2}) can have different values and has to become negative if the droplet radius (R_d) becomes twice as large as the fixed curvature (R_{p1}) on the plateau, due to the decrease of the pressure in the growing droplet. We can describe this balance with:

$$\frac{2\sigma}{R_d(t)} = \frac{\sigma}{R_{p_1}} - \frac{\sigma}{R_{p_2}(t)}; \quad \text{if} \quad R_d > 2R_{p1}, R_{p2} < 0 \qquad (2)$$

In the close-up movies (Figure 3), we observed that the curvature in the x-y plane R_{p_2} indeed becomes more and more negative in time, which underpins the explanation of the observed interfacial behavior. With the forced decrease in R_{p2}, a quasi-static neck near the edge is created because the Laplace pressure in the droplet, and thus neck, does not change very rapid anymore with the growth of the droplet. As long as the amount of oil flowing into the droplet does not exceed the amount of oil flowing into the neck from the surrounding area on the plateau, the droplet will remain attached otherwise the neck will break.

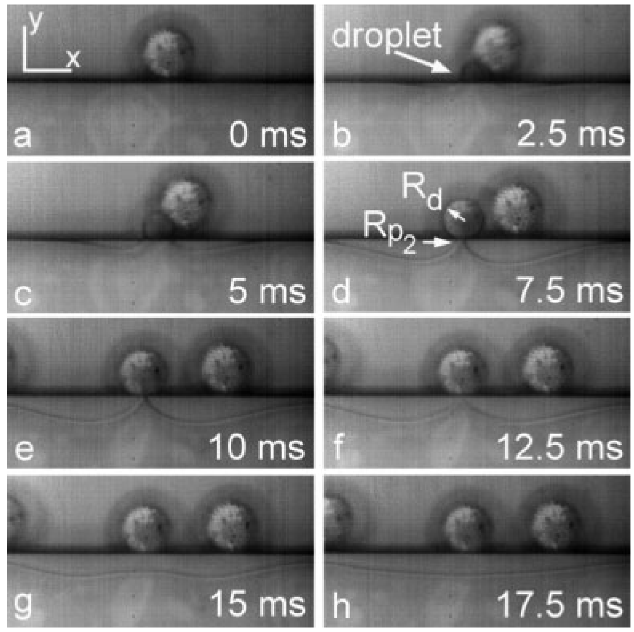

Figure 3. Droplet formation in an EDGE-2.6 device.

In image a, the plateau is completely filled with oil, and in image b, the forming droplet becomes visible, and in the subsequent images, the droplet grows and is connected through a neck to the plateau, until in image g, the neck breaks and a droplet is released.

This description also implies that the pressure dependency of the droplet size should not be very strong, unless blow-up of the neck occurs. This is investigated experimentally for both EDGE systems (Figure 4); D_{drop} is in this case determined with image analysis software (ImagePro Plus), and 100 droplets have been measured. To make comparison between both systems easier, the dimensionless droplet diameter D, defined as the droplet diameter D_{drop} divided by the height H_p of the DFU, is plotted vs. the dimensionless applied pressure (the ratio of applied pressure and minimal pressure necessary to invade the plateau). At low pressures, D seems constant (around 6 H_p); possibly, a very small increase could be noted, only when a certain pressure is exceeded the droplet size increases very rapidly.

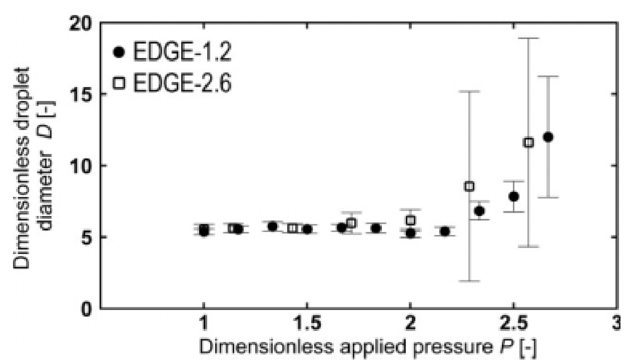

Figure 4. Dimensionless droplet diameter of emulsions produced with the EDGE-1.2 and EDGE-2.6 systems as a function of the dimensionless applied pressure.

The main factor that determines the droplet diameter in the pressure independent range (Figure 4) is the height of the plateau, (as mentioned, a scaling factor of 6 is found), and further investigation is necessary to elucidate this factor in detail. Compared with scaling factors reported for other microchannel systems, (2.5–4 times the smallest channel dimension), the values here are higher.

The droplet size generated by EDGE is not very sensitive to pressure changes and that is a big benefit compared with other microtechnological emulsification devices. Further, problems that are mentioned in literature for other systems, e.g., fabrication accuracy (microchannels), flow conditions (any shear based technique), and pressure distributions (up-scales microsieves or microchannels) are unlikely to happen. The large plateaus are not a serious a challenge for the modern etching techniques. In addition, each DFU can be considered as self-regulating; the droplet formation position along the edge is not forced to be on a specific spot but can be anywhere and at many places at the same time. Besides, we noted that operation of the plateaus was straightforward; after pressurization, the plateaus fill with oil, and even if some disturbing factor (e.g., a speck of dust) is present, which influences the flow pattern, the wide plateau system fills regularly. Overall, the system is very stable, which is essential for any practical application, and we expect EDGE to be a promising candidate for scale up.

Away from water-in-oil emulsions, the mechanism presented here is expected to be suitable for double emulsions (water-in-oil-in-water) and for the production of foam. If hydrophobic chips become available, it is also expected that W/O emulsions can be produced.

In summary, we have shown a new microfluidic droplet formation unit which simultaneously produces multiple micron-sized droplets with a narrow size distribution. Interfacial tension is the driving force for the process and the observed behavior can be described with basic physical laws. We believe that this EDGE-system is very suitable for scale up, which could be of great significance for further development of mild emulsification processes.

Acknowledgments

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