MASSIVELY-PARALLELIZED PRODUCTION OF FEMTOLITER DROPLETS AND ITS APPLICATION TO SELF-ASSEMBLED NANOPARTICLE CLUSTERS FOR NOVEL METAMATERIALS.

Corentin B.M. Tregouet[1], Chris L. Kennedy[2], Ramkrishna Kotni[2], Sofie Kölling[3], Johan G. Bomer[3], Jasper J.A. Lozeman[3], Detlef Lohse[4], Albert van den Berg[3], Alfons van Blaaderen[2], and Mathieu Odijk[3*]

[1]Soft Matter Department, Institut de Physique de Rennes, Université Rennes 1, France
[2]Soft Condensed Matter, Debye Institute for Nanomaterials Science, Utrecht University, the Netherlands
[3]BIOS-Lab-on-a-Chip group, MESA+ Institute for Nanotechnology, TechMed Center, Max Planck Center for Complex Fluid dynamics, University of Twente, the Netherlands
[4]Physics of Fluids group, MESA+ Institute for Nanotechnology, TechMed Center, Max Planck Center for Complex Fluid dynamics, University of Twente, the Netherlands

ABSTRACT

Recently, a new method has been developed to produce large monodisperse population of droplets. Key is to ensure a droplet diameter independent of the flow rate in each parallel channel. This chip, the Millipede, raises high hope, but is limited to large droplets. Here we present a glass microfluidic chip, the Nanopede, designed on the same principle, downscaled to produce femtoliter droplets (diameter 1µm). Prior to chip design, theoretical analysis of flow and destabilization has been performed. Finally, this chip has been used to lead self-assembly experiment within these nanodroplets, a first step toward hierarchically organized metamaterials.

KEYWORDS: Microfluidics, Parallelization, Droplets, Step emulsification, Self-assembly, Metamaterials.

INTRODUCTION

Droplet-based microfluidics has achieved a lot in the past two decades. A new family of devices has been developed in the last few years which ensure parallelization of droplet production with a droplet diameter independent of flow rate on a large range of flow rates [1,2]. Therefore, the interaction between the different devices does not affect monodispersity. Consequently, this method raises high hope for large scale production of finely-controlled emulsions. Nevertheless, the droplet size, fixed by the geometry of the device, remains too large for a large range of applications. Downscaling the previously presented devices raises technical and fundamental challenges.

In this paper, we present a new glass chip which has been designed following the same principle as the Millipede [1] to produce large quantities of femtoliter droplets (diameter around 1µm): prior to design and production, theoretical analysis of destabilization and flow in this regime has been performed to ensure uniform production, high production rate, in a reasonable range of applied pressure. We will introduce the main features of this new chip which we called the Nanopede, and we will present first results we obtained in the creation of ordered metamaterials.

EXPERIMENTAL

To ensure that the flow rate between the different nanochannels is homogeneous, the hydrodynamic resistance of the nanochannel has to be high compared to the resistance of the feeding channel between two neighboring nanochannels and the drain channel. The maximum flowrate variation between the first and last nanochannel has been fixed to 5%, which yields conditions for the nanochannel dimensions. The destabilization time of the droplet cannot be calculated according to the prediction of the Millipede [1]. Indeed, with this size change, viscosity and inertia must be both considered to calculate the break-up time [3].

Following these recommendations, glass chips have been produced with wet etching and deep reactive ion etching (Figure 1a). Emulsification occurs where the nanochannels conveying the dispersed phase are connected to microchannels which contain the continuous phase, as sketched in Figure 1b. The nanochannels have a height of 200 nm and are about 1 µm wide, while the microchannels are 15 µm deep, as shown in Figure 1c. In one chip, 5 devices are operating in parallel, each of them consisting in 1000 nanochannels. Lateral inlets and outlets enable easy injection of the suspension and extraction of the emulsion.

RESULTS AND DISCUSSION

This chip enables the production of large quantities of droplets of diameter close to 1 µm (100 µL of hexadecane dispersed in 1mL of water) while preserving a very high monodispersity, as shown in Figure 2a-b, without the need of an active feedback loop on the pressure flowrates. The chip was then used to produce droplets of cyclohexane containing ferromagnetic nanoparticles of 10 nm diameter. Evaporation of cyclohexane compresses the nanoparticles in a spherical confinement, resulting in the aggregates presented in Figure 2c. Production of very large quantities of monodisperse aggregates of nanoparticles paves the way towards the production of multiscale hierarchically-organized metamaterials with remarkable optical and electro-magnetical properties.

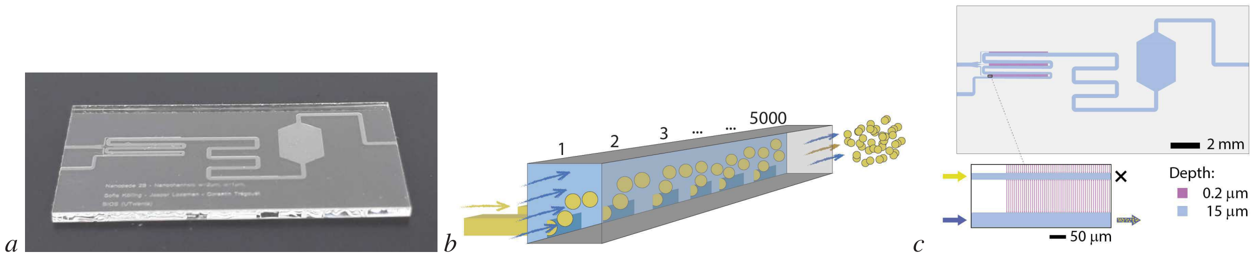

Figure 1: a- Picture of the glass microfluidic chip. Dimensions are 30 mm by 15 mm. b- Emulsification occurs at the connection between the nanochannels (dispersed phase) and the microchannels (continuous phase). c-Schematic of the chip with the different depth and phases (oil in yellow arrow, water in blue arrow).

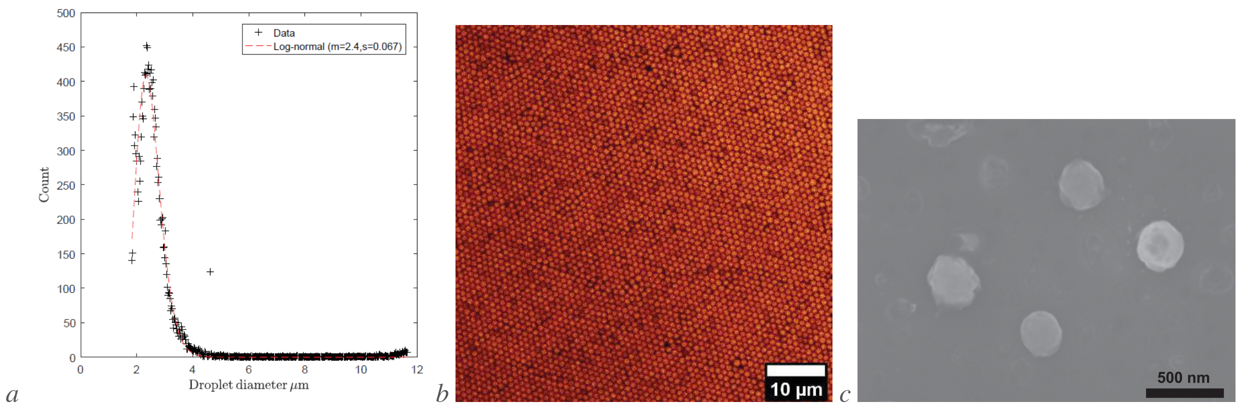

Figure 2: a- size distribution of hexadecane droplets in water with sodium dodecyl sulfonate, following a log-normal law (mean value and standard deviation in legend), b- confocal image of the resulting emulsion which shows crystals of droplets due to the high monodispersity; c- scanning electron microscopy (SEM) image of the ferromagnetic-nanoparticle aggregates.

ACKNOWLEDGEMENTS

This work was supported by the Netherlands Center for Multiscale Catalytic Energy Conversion (MCEC), and the Netherlands Organisation for Scientific Research (NWO) Gravitation program funded by the Ministry of Education, Culture and Science of the government of the Netherlands.

REFERENCES

[1] Amstad E., Chemama M., Eggersdorfer M., Rodriguez Arriaga L., Brenner M. P., Weitz D. A. "Robust scalable high throughput production of monodisperse drops." *Lab Chip*, 2016 **16**, 138–155.

[2] Ofner A., Moore D. G., Rühs P. A., Schwendimann P., Eggersdorfer M., Amstad E., Weitz D. A., Studart A. R. "High-Throughput Step Emulsification for the Production of Functional Materials Using a Glass Microfluidic Device." *Macromolecular Chemistry and Physics*, 2017, **218**,1–10.

[3] Driessen T., Jeurissen R., Wijshoff H., Toschi F., Lohse D. "Stability of viscous long liquid filaments." *Physics of Fluids*, 2013, **25**, 062109.

CONTACT

* M. Odijk; m.odijk@utwente.nl