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COMMENT

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# Reply to the 'Comment on "Wetting-induced formation of controllable monodisperse multiple emulsions in microfluidics"' by J. Guzowski and P. Garstecki, *Lab Chip*, 2014, 14, DOI: 10.1039/C3LC51229K

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In their comment, Guzowski and Garstecki pointed out an error in our paper concerning the assumption that drops of one phase will completely engulf other drops to form multiple emulsions when the complete engulfing configuration has a lower energy than that of the non-engulfing configuration.[1] Indeed, partial engulfing may have a lower energy than both complete engulfing and non-engulfing, and this should not be neglected.

As reported by Torza and Mason in 1969,[2] when two immiscible drops $i$ and $j$ disperse in a third immiscible fluid $k$, the spreading coefficients can be described as $S_i = \gamma_{jk} - (\gamma_{ij} + \gamma_{ik})$ when the final equilibrium states of the three phases are determined solely by the three interface tensions. When $S_i > 0$, drop $i$ can completely engulf drop $j$ to form a double emulsion drop. They also concluded that the topologies of the three immiscible systems are independent of the volumes of the drops,[2,3] which was also confirmed by Guzowski and Garstecki with the Surface-Evolver software.[4]

In our study, we utilized complete engulfing of water drops (A) and oil drops (B) including A-engulfing-B and B-engulfing-A to prepare different types of multiple emulsions in microfluidics. The whole engulfing process was performed in an immiscible fluid (C) flowing in a chamber of microchannels. The interfacial tensions of the A-engulfing-B systems are, surprisingly, not in accord with the reported criteria that drop $i$ can completely engulf drop $j$ only if $S_i > 0$. According to the reported theory, the combination of the applied fluids makes the spreading coefficients negative ($S_i < 0$, $i$ = A, B, C), resulting in partial engulfing, as predicted in the comment by Guzowski and Garstecki. However, our experiments show a complete engulfing in the chamber of microchannels (Fig. 1e, h, i and 4e, f, g in our paper), and the whole process of engulfing was totally spontaneous.

We also believe that the equilibrium topology of double droplets depends only on the three interfacial tensions, and that other parameters, such as drop sizes, gravity, fluid motion, *etc.*, do not determine the position of equilibrium. However, if drops are dispersed in a flowing fluid, the interfacial tensions between the drops and the carrier fluid as well as the drop shapes will be influenced by many factors including the drop sizes, microchannel geometries, and fluid motion (Fig. 1). Certainly, transformation of drop shapes and internal circulation flow within drops can greatly impact the effective local interfacial tensions of the system. Therefore, the behavior of drop engulfing under flowing conditions may be different from that under quiescent conditions. We believe that the size of the drops has some impact on the engulfing process in microchannels because the systems are in a state of flow. Unfortunately, these effects are too complex to be predicted by a well-defined equation at present.

In their comment, Guzowski and Garstecki used the simulation software Surface Evolver to determine the equilibrium morphology of a double droplet using the parameters reported in our paper. Partial engulfing is evaluated as the equilibrium topology in their numerical calculations. However, the complete engulfing of phase A2 by phase B was successfully performed in our experiment as shown in Fig. 1e, h, i and 4e, f, g

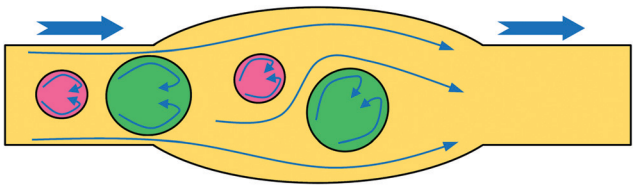

**Fig. 1** Local circulation flow occurs within the droplets when the droplets flow through microchannels.

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in our paper as well as in Movie 2 in the ESI (ref. 1). All of the experiments of drop engulfing in our study were carried out in a flowing fluid in microchannels. This flowing condition could considerably change not only the shapes of drops but also the interfacial tensions of the systems, which could promote drop engulfing in microchannels. As a consequence, we conjecture that there are two main causes that induce complete engulfing: The first is the influence of the fluid motion and the resultant change in the shapes of the drops. The second is that when $\lim S_B \to 0^-$ drop B also could wet drop A2 completely to form an A2/B/C double emulsion drop (for more details, please see ref. 3). In our experiments, we find $S_B = -0.49$. Accounting for possible experimental errors in the interfacial tensions, the limit of $S_B$ is close to zero as well. This is, perhaps, why the A2/B/C double emulsions that we prepared remain stable (Fig. 4g in the paper). However, we here clarify that the freshly prepared multiple emulsions whose system does not agree with the criterion ($S_i > 0$) may not be at their final equilibrium states, and may transform into other topologies due to dewetting.

In addition, eqn (1)–(4) in our paper, based on the incorrect assumption, are also incorrect. In general, only if $S_i > 0$, where $S_i = \gamma_{jk} - (\gamma_{ij} + \gamma_{ik})$, will drop $i$ completely engulf drop $j$ to form a stable multiple emulsion.

The corrections do not change any of the conclusions in our paper, specifically that multiple emulsions are successfully created from wetting-induced drop-engulfing-drop phenomena by mixing lower-order emulsions together. Corrections to this paper have been published in *Lab on a Chip*.

The authors apologize for the mistakes in our paper and for any inconvenience caused. The authors also greatly appreciate Dr. Jan Guzowski and Prof. Piotr Garstecki for pointing out this error.

## References

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