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COMMENT

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Comment on "Wetting-induced formation of controllable monodisperse multiple emulsions in microfluidics" by N.-N. Deng, W. Wang, X.-J. Ju, R. Xie, D. A. Weitz and L.-Y. Chu, *Lab Chip*, 2013, 13, 4047

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In their recent work, Deng *et al.*[1] stated that the equilibrium topology of double droplets depends on the volumes of the immiscible segments (page 2, the text above eqn (1)). This statement was not verified by the experimental results in ref. 1 yet it was used in the discussion and interpretation of the data.

We believe that it is important to make it clear that the volumes of the constituent segments do not determine the topology of double droplets. Such dependence would stand in clear contradiction to our recent findings[2] as well as to the previous studies by Torza and Mason[3] or Pannacci *et al.*[4] and might lead to confusion in the interpretation of experimental results concerning multiple emulsions.

The statement in ref. 1 arises from the assumption, expressed quantitatively in eqn (1), that if the complete engulfing configuration has a lower energy than the non-engulfing one, then the former must be the equilibrium topology. This assumption omits the case of partial-engulfing (although the article does show such a configuration in Fig. 1a2) that might lead to an even lower energy than the other two topological configurations and as such might be the equilibrium topology. Following this assumption, the authors defined a volume-dependent 'spreading coefficient' in eqn (4) (usually defined only in terms of interfacial tensions) and used it to determine the equilibrium topology (page 2, the text below eqn (4)).

In reality, the topology of multiple droplets is determined by the equilibrium contact angles at the three-phase contact line between the immiscible segments. The values of these contact angles are in turn fully determined by the interfacial tensions between the phases. Thus, a change of the volumes of the segments cannot lead to a change of the topology. The general conditions of mechanical equilibrium at the contact line can be geometrically expressed in terms of the so-called Neumann's triangle (see, *e.g.*, Fig. 1a in ref. 2), which implies the following formula (eqn (3) in ref. 2) for the contact angles θ_i, as measured in the i-th phase:

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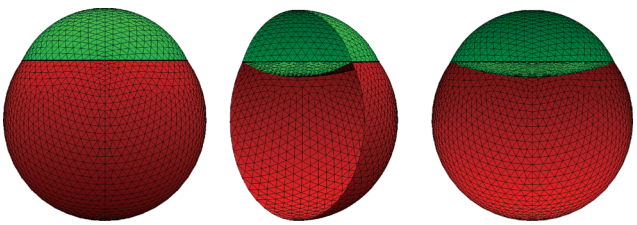

Fig. 1 Visualizations of the numerically calculated shape of a double droplet (with phase A2 marked in red and phase B in green) for the values of the interfacial tensions and the ratio of volumes taken from ref. 1 in which Deng *et al.* claimed complete engulfing of phase A2 by B.

$$\cos\theta_i = \frac{\gamma_{jk}^2 - \gamma_{ik}^2 - \gamma_{ij}^2}{2\gamma_{ik}\gamma_{ij}},$$

where i = A, B and C, and $i \neq j \neq k$. The transition between the topologies occurs whenever $\cos\theta_i = -1$ or $\cos\theta_i = 1$. This condition reduces to $S_{i,\mathrm{Torza}} = 0$ with the volume-independent spreading coefficient defined by Torza and Mason[3] as $S_{i,\mathrm{Torza}} = \gamma_{jk} - \gamma_{ik} - \gamma_{ij}$. Accordingly, *e.g.* for $S_{\mathrm{A,Torza}} > 0$, phase A completely wets the interface between phases B and C, which corresponds to complete engulfing of drop B by drop A, independent of the volumes of the segments.

To illustrate this point, we carefully examined the case studied experimentally by Deng *et al.* in which the interfacial tensions between the droplet phases A2 and B and the external phase C were $\gamma_{\mathrm{A2C}} = 3.16$ mN m^{-1} and $\gamma_{\mathrm{BC}} = 3.07$ mN m^{-1}, respectively, and the interfacial tension between the droplet phases was $\gamma_{\mathrm{A2B}} = 0.58$ mN m^{-1}. On page 3 (and repeatedly on page S3 in the ESI) the authors claimed that these values "(…) make the spreading coefficient of the water phase (B) over the soybean oil phase (A2) (S_{B}) positive if the drop size ratio of $R_{\mathrm{B}}/R_{\mathrm{A2}}$ is larger than 0.49 (…)."

Following this analysis, the article suggests complete engulfing of phase A2 by phase B. We used the Surface Evolver to determine the equilibrium morphology of a double

droplet assuming the above given interfacial tensions and the ratio of droplet radii $R_B/R_{A2} = 0.6$, such that $R_B/R_{A2} > 0.49$ and $S_B/\gamma_{A2B} = 0.19 > 0$ (with S_B defined in eqn (4) in ref. 1). We note that for such a choice of the interfacial tensions the spreading coefficient as defined by Torza and Mason[3] equals $S_{B,Torza}/\gamma_{A2B} = -0.49 < 0$, which corresponds to partial engulfing. Indeed, in our numerical calculations (Fig. 1) we found partial engulfing as the equilibrium topology. This result provides a direct counterexample for the reasoning provided by Deng *et al.* in ref. 1.

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