TWO-PHASE DROPS IN MICROFLUIDIC DEVICE

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ABSTRACT

We report experimental and theoretical studies of double droplets produced in microfluidic systems. Standard soft-lithography with poly(dimethylsiloxane) (PDMS) is used for the device fabrication; the geometry is a double flow focusing. In theory, morphologies of double droplets are determined by spreading parameters involving surface tension. The comparison between the morphologies predicted thanks to surface tensions measurements and the objects produced in the microfluidic device is done for more than thirty triplets of fluids. It is shown that as a whole the observed morphologies (complete engulfing, partial engulfing and non engulfing) on long time scales are solely controlled by fluid interfacial energies and therefore can be predicted independently of the geometry and the surface properties of the microsystem. Non-equilibrium long lived double droplets, are observed in the flow just after their formation such as complete engulfing (a droplet in a drop) even if the stable state is different. A simple hydrodynamic theoretical model based on Hadamard Rybzyński analysis estimates the lifetime of these metastable structures assuming recirculations are responsible the displacement of the internal droplet in a drop. We cured the objects in the metastable state in order to illustrate microfluidic technology allows the synthesis of particles impossible to produce with standard technologies.

1. INTRODUCTION

Double emulsions (i.e. emulsions in which the dispersed phase is also an emulsion) are of considerable interest in food and cosmetic industries, in medical sciences (drug delivery), in printing and textile industries [1]. In most cases, double emulsions provide elegant solutions for the controlled release of chemical species in a complex medium. Traditional techniques of production of double emulsions essentially consist in mixing three fluids together. This naturally leads to obtain broad size distributions and a substantial variety of morphologies. The development of microfluidic technology [2-3] offers new opportunities for producing double emulsions with sharp and predictable characteristics. Production of double emulsions in microfluidic systems [4-5-6] and in capillaries [7] has already been demonstrated. In comparison to traditional methods, microfluidic technology obviously improves the control of the morphology of the double emulsions, reduces the size dispersivity, and facilitates the control of the number of droplets inside each host drop. Still, it would be desirable to know which type of double-drop morphology can be expected in a given microfluidic experiment, and to which extent this may depend on the geometry and the physico-chemical properties of the walls that confine the fluids. This issue, which is crucial for the development of the domain, has not been addressed yet. We will show that the stationary structures that are obtained are solely controlled by fluid interfacial energies and therefore can be predicted independently of the geometry and the surface properties
of the microsystem. Moreover, we could controllable produce non-equilibrium long-lived double droplets, a possibility that opens the way to generate objects impossible to produce with standard technologies.

2. EQUILIBRIUM MORPHOLOGIES

We start with the theory: equilibrium theory states that, in infinite media, the morphologies adopted by three immiscible liquids correspond to a minimum in the total interfacial energy of the system [8]. Formally, the definition of the equilibrium is more directly expressed in terms of the spreading coefficient 

\[ S_i = \gamma_{jk} - (\gamma_{ij} + \gamma_{ik}) \]

where \( \gamma_{ij} \) are the interfacial tensions between fluid \( i \) and \( j \). Choosing the fluids so as \( S_1 < 0 \), Fig. 1 shows the three distinct morphologies that equilibrium theory predicts: complete engulfing, partial engulfing (called “Janus”), and non-engulfing. Experimental studies on mixtures of immiscible fluids indicate that, as a whole, this theory provides predictions that are consistent with the observations [9].

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**Figure 1**: Three possible equilibrium morphologies according to the sign of spreading coefficient values: complete engulfing (\( S_1 < 0, S_2 < 0, S_3 > 0 \)), partial engulfing (\( S_1 < 0, S_2 < 0, S_3 < 0 \)) and non-engulfing (\( S_1 < 0, S_2 > 0, S_3 < 0 \)).

We now come to the experiments: the experimental systems we use are made of poly(dimethylsiloxane) (PDMS) using soft lithography technique [10]. The microchannels have a double flow focusing geometry (Fig. 2) consisting of two consecutive crossjunctions. In such a geometry, an emulsion of A/B is produced at the first cross-junction. It is then transported downstream in a channel, and at the second cross-junction, by the in-flow of fluid C, the double emulsion A/B/C is formed. The microchannels have rectangular cross sections, typically 100 \( \mu \)m deep and 200 \( \mu \)m wide, with a length of 2 cm for the main channel. The main channel ends in a chamber. In most cases, the microsystem is sealed after a 30 s exposure in an oxygen plasma cleaner (Harrick). The consecutive hydrophilic property of the PDMS microchannels [11] permits then to produce direct oil in water (O/W) emulsions [12]. In other cases the PDMS was hydrophobic (the hydrophobic recovery is accelerated in an oven) it then allows inverse emulsion (W/O) formation.

The fluids we worked with are alkanes, octanol, rapeseed oil, fluorinated oil, mineral oil, silicone oil, tripropylene glycol diacrylate (TPGDA) and water with and without surfactant (SDS 1% w/w). Chemical products are commercial ones (Sigma, Aldrich, VWR, CRC Industries) with a purity grade of 99%, and we performed the experiments without any further purification. The three surface tensions corresponding to the three possible interfaces are measured by the pendant drop method and the ring technique. We systematically mix the three fluids together before performing the measurements so as to establish interfacial surface tension measurements in conditions where the equilibrium is reached, driven both by surface energies and the solubilities of the various phases in contact. Mixing prior to interfacial tension measurement turned out to be crucial when impurities in a liquid can act as a surfactant for the two other fluids or when fluids show significant partial solubilities.

Figure 2: Double flow focusing geometry: a first emulsion A/B is produced upstream. Further downstream fluid C engulfs the emulsion, and the double emulsion A/B/C is formed. On the bottom right is shown the observation chamber.

Figure 3: Two pictures of double-droplet experiments. To the left, a partial engulfing with silicone oil and rapeseed oil in distilled water. To the right, a complete engulfing with fluorinated oil/silicone oil/water+SDS in a stable state (no flow). The white scalebars are both 100 µm.

To produce double emulsions, we drive the three fluids into the microsystem, tuning pressure or flow rates so as the droplets are formed sequentially at the first and second junctions. Typical orders of magnitude are 10 µL min⁻¹ for the flow rates and 100 mbar up to the atmospheric pressure for the applied pressure. The corresponding Reynolds numbers Re are smaller than 2 and the capillary numbers Ca are below 2 × 10⁻⁴. Here, by definition, \( Ca = \frac{\mu U}{\gamma} \), where \( \mu \) is the dynamic viscosity of the outer phase, \( U \) the velocity of the drop and \( \gamma \) the interfacial tension between the drop and the continuous fluid. In order to achieve equilibrium, the flow is interrupted by squeezing the outlet tube along with stopping the syringe pumps. The morphology of the double droplet is then observed in the chamber; its stability is observed for half an hour up to fifty hours.

In Fig. 3 two pictures of crystal of Janus and complete engulfing droplets are shown, while the diagram of spreading parameters in Fig. 4 summarizes the results we obtained for thirty triplets of fluids along with the theoretical expectations. In this diagram, there exists mathematically forbidden regions, represented on the graph. The dashed line represents the limit induced by Girifalco model [13],

\[
\gamma_{12} = \gamma_1 + \gamma_2 - 2\Phi \sqrt{\gamma_1 \gamma_2} \quad (1)
\]
Figure 4: Comparison between predicted and observed morphologies: squares represent observed non-engulfing, disks observed engulfing and triangles observed partial engulfing. The dotted line shows the limit for $\phi = 0.92$ according to Girifalco’s formula (1).

where $\gamma_{ij}$ is the interfacial energy between interface $i$ and $j$, $\gamma_i$ is the surface tension of liquid $i$ (i.e. against air), and $\phi$ a coefficient close to unity. For illustrative purposes Girifalco’s limit is drawn here for $\phi = 0.92$. As a whole, Fig. 4 shows that our observations are in agreement with the predicted morphologies, in particular when the spreading coefficients $S_2$ and $S_3$ are well above the experimental uncertainty on the surface tension measurements which we estimate here to be on the order of $\pm 1$ mN/m. Agreement between theory and experiment is more questionable at low values of $S_3$, i.e. close to the theoretical boundary between Janus and complete encapsulation. In particular, we observed a trend, where systematically, Janus are located slightly above the horizontal axis. One may speculate that this trend results from the existence of two-dimensional films at the interfaces or any cause which may lower the spreading coefficient $S_3$ by a couple of mN/m. Nonetheless, the discrepancy that we point here is close to the experimental uncertainty. Thus one may conclude that as a whole, the diagram of Fig. 4 agrees with the theoretical expectations. Equilibrium theory thus appears as a valuable starting point to analyze morphologies produced in microsystems, independently of the way the structures are produced and the geometry and surface properties of the walls.

3. NON-EQUILIBRIUM MORPHOLOGIES

We now turn our attention to the non-equilibrium morphologies that are typically observed between the formation section and the reservoir. Two examples of non-equilibrium shapes are shown in Fig. 5. In the first case, complete engulfment is observed, while the corresponding equilibrium morphology obtained in the chamber by arresting the flow, is a Janus state. The second case also shows complete engulfing, while non-engulfing is the equilibrium state. In fact, the dynamics towards equilibrium can be classified into two types. In the first type, the three interfaces are physically in contact with each other through a contact line, just after the structure is formed. In this case, the time it takes to reach equilibrium in such a case is less than 0.1 ms, which is comparable to the capillary time $\tau_c = \mu L / S$ where $L$ is the characteristic size of the object and $S$ a spreading coefficient. In the second type, the three fluids have no contact line in common after formation of the structure: a small droplet inside a larger host droplet. In this case, we observe an evolution towards equilibrium on a time scale on the order of hundreds of milliseconds, i.e. several orders of magnitude above the capillary time scale. In this case, the system evolves slowly until a contact line appears, when the inner droplet touches the inner
boundary of the host droplet, triggering the fast evolution towards a morphology close to that observed at equilibrium.

Figure 5: a) Morphology evolution from a complete encapsulation just after formation to a janus; fluids are tetradecane/TPGDA/water+SDS. b) Different morphologies for fluorinated oil/water+SDS/TPGDA, stable state is on the right. The white scalebars are both 100 µm.

Here we analyze the case where the system evolves from a complete encapsulation to a Janus equilibrium state. We measured the distance \( d \) between the center of the inner droplet and the interface of the host droplet, versus time measured from the moment when the three fluids leave the second cross-junction. In Fig. 6 the reduced distance \( d/a \), \( a \) being the radius of the host droplet, for three different experiments is plotted versus the reduced time \( t/\tau \), where \( \tau \) is the time it takes for the inner droplet to touch the interface of the host droplet. We could check the trajectory of the droplet is close to a diameter, parallel to the main stream. In the three cases, \( \tau \) ranges between 0.68 and 1.29 s, and the dynamics of the process is roughly linear in time. We present a model which may be used as a starting point to estimate the life-time of non-equilibrium engulfing morphologies in situations where the equilibrium state is a Janus. The model is based on the idea that the droplet is displaced under the action of internal recirculations in the host drop. In the model, it is assumed that the droplet behaves as a small neutrally buoyant particle advected by the internal flow.

In order to model the flow, we use low Reynolds number Hadamard-Rybzynski analysis [14-17] of a drop of radius \( a \), of viscosity \( \hat{\mu} \) moving with steady velocity \( U \) along the x-axis inside a surrounding liquid of viscosity \( \mu \). The flow model we use here is consistent with the experimental and numerical work of Ref. [18]. Choosing a coordinate system with its origin at the steady moving center-of-mass of the drop, introducing the viscosity ratio \( \lambda = \frac{\hat{\mu}}{\mu} \), the relative velocity \( V \) of the droplet is given by:

\[
V = \frac{dx}{dt} = \frac{1}{2(1+\lambda)} \left( 1 - \frac{x^2}{a^2} \right) U \tag{2}
\]

We define the displacement time \( \tau_{th} \) as the time it takes for the inner droplet of radius \( \hat{a} \) to move along the center axis from the center \( x = 0 \) to the interface \( x = a - \hat{a} \) of the host drop, and using Eq. (2) we obtain

\[
\tau_{th} \approx \int_0^{a-\hat{a}} \frac{dx}{V} = (1 + \lambda) \ln \left( \frac{2 - \alpha}{\alpha} \right) \frac{a}{U} \tag{3}
\]

As expected, \( \tau_{th} \) diverges for \( \lambda \to \infty \). A typical example is shown in Fig 6. In practice, the displacement is close to be linear in time, consistently with the experiment.
When inserting the experimental values for $\lambda$, $\alpha$, a and $U$ in Eq. (2) we obtain a predicted displacement time $\tau_{th}$ ranging between 0.07 s and 0.22 s, i.e. between three times and one order of magnitude smaller than the experiment. The theory underestimates the actual duration of the transient state, probably due to the fact that the microchannel walls and to the perturbation of the internal circulation caused by the host droplet are neglected in the theory. Nonetheless, the theoretical model roughly captures an order of magnitude for the life-time of the non equilibrium structure and thus may be used as a starting point.

![Figure 6](image_url)

**Figure 6**: Reduced distance $d/a$ from the center of the inner droplet to the interface of the host drop versus reduced time $t/\tau$ after the double emulsion formation. Open circles, circles and triangles are respectively for experiments a, b and c, with experimental parameters $a = 65 \mu m, 98 \mu m, 92 \mu m; \dot{a} = 26 \mu m, 37 \mu m, 40 \mu m; \alpha = 0.4, 0.38, 0.43; U = 20.4 \text{ mm/s}, 10.3 \text{ mm/s}, 9.3 \text{ mm/s}$. For experiments a, b and c, the viscosity of the inner droplet is $\mu_0 = 3 \text{ mPa s}$, the viscosity of the drop is $\mu = 15 \text{ mPa s}$; the viscosity of the carrier is $\mu = 1 \text{ mPa s}$ for experiments a and b and $2.4 \text{ mPa s}$ for experiment c due to addition of glycerol. The viscosity ratio is thus $\lambda = 15$ for experiments a and b and $\lambda = 6.2$ for experiment c. The measured times for the morphology to evolve from a complete engulfing one to a jansus one are $\tau = 0.68 \text{ s, 0.78 s, and 1.29 s}$, respectively. The line shows the theoretical prediction based on the parameters of experiment c.

In practice, the lifetime of the non equilibrium engulfed state allows to produce new particles. This is shown in Fig. 7 in which we used a photocurable polymer as one of the three working fluids. We could photocure this monomer in less than 100ms, using a technique similar to [19]. Figure 7 shows that the same system, with the same flow conditions, generate fully encapsulated particles at early times (Fig. 7a) and Janus particles at longer times (Fig. 7b). This illustrates the advantage one can draw out from the excellent control of the kinetics of formation offered by microfluidic technology.

![Figure 6](image_url)

**Figure 6**: SEM pictures of two different morphologies obtained with the same fluids, in the same chip, and cured under UV light: (a) non equilibrium structure (cut with a razor blade so as to reveal full encapsulation) (b) equilibrium structure in form of Janus particle. The fluids are tetracane, acrylate monomer + 8% Darocur and water + 1% SDS.
4. CONCLUSIONS

In conclusion, the experiment shows for the first time that despite the importance of the confinement in miniaturized systems, the morphologies that can be obtained in such systems satisfy equilibrium conditions. The analysis of thirty triplets of fluids indicates that equilibrium theory predicts shapes in excellent consistency with the experiment. In the same experiment, we could generate reproducible non equilibrium shapes whose life time is long enough to work with (for instance, to cure so as to produce solid objects). Microfluidic technology thus allows to generate controlled double drop structures that would be impossible to obtain by using standard techniques, thus opening a pathway towards the formation of entirely novel objects, in the micrometric range.

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