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Selective emulsion inversion in an equilibrium Janus drop. 1. Unlimited space

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ABSTRACT

The potential for a catastrophic inversion of one phase in a Janus emulsion drop was investigated by local equilibrium calculations of a single Janus drop of two mutually insoluble oils, O1 and O2, in an infinite aqueous continuous phase, (O1 + O2)/W. The relative volume of the oil with less interfacial tension towards water, O2, was increased, while the radius of the O1 part of the drop was held constant at unity. The limiting fraction of O1 covered by O2 was calculated for infinite O2 volume for a selected interfacial tension combination. After the O2 volume reached infinity, the volume of the continuous aqueous phase was reduced to finite values, leading to a selective inversion of the emulsion from (O1 + O2)/W to (W + O1)/O2. Thenceforward, further removal of the water led to an additional reduction of the size and radius of the water cap.

1. Introduction

Emulsions [1] are an important part of colloid systems, due to the many questions and problems arising from the multiple facets of their formation [2] and the multitude of problems concerning stability [1]. Multiple emulsions [3] early attracted significant interest, to a large degree because of industrially vital applications [3], of which the nanoparticles as stabilizers are an essential component [4]. The recent introduction of the microfluidics process [5] lead to a radical increase of the research on double emulsions, partly because of interesting novel applications [6] as reviewed by Guzowski et al. [7] and Neeson et al. [8]. Bormashenko [9] has recently been introduced a new and elegant method to prepare Janus drops [10,11]. Small (10–20 μl) water drops were rolled on a fine powder of polytetrafluoroethylene or carbon black deposited on a super-hydrophobic surface, giving drops covered either by PTFE or carbon black. When two drops, each covered with one of the powders, were brought in contact, they united to a Janus drop hemi-spherically covered by each powder. The drops remained stable, when deposited on solid and liquid water supports, but broke up along the plane separating the PTFE/carbon black plane, when punctured with a needle.

The topology of Janus drops from microfluidics preparation is based on local interfacial equilibrium at the three-liquid contact line [7], as demonstrated in an elegant recording [12], in which a double emulsion drop of tripropylene glycol diacrylate in tetradecane in a 1% aqueous solution of sodium dodecylsulfate was allowed to equilibrate into a Janus drop configuration. The correlation between topology and interfacial tensions subsequently was comprehensibly tested in micro-fluidics experiments by Guzowski et al. [7] giving topologies in excellent agreement with predictions from interfacial tension [7,8,12] calculations. The evaluations [7,12] were restricted to the topology of the Janus drop per se; the activity of the continuous phase was limited to its contributions to the interfacial tensions between the liquids. In summary, the anticipated agreement is well confirmed between the topology of the Janus drop per se, as found in the microfluidics experiments and the one from calculations based on local equilibrium at the contact line.

In the recent discovery that Janus emulsions also can form in a one-step process using the traditional high energy emulsification [13–15] gave an unanticipated result. The Janus emulsions formed under these turbulent conditions showed drop topology close to the one expected from interfacial tension equilibrium, in spite of the high energy input in the process, including a final shear between the microscope slide and the cover glass. This circumstance encouraged preliminary investigations [16,17] on the potential effect of interfacial tension for the drop topology of the specific emulsion system [13–15], notwithstanding details of the formation of these emulsions still under investigation. In this context, it is essential to notice the later report [18] on the preparation of Janus emulsions in a one-step microfluidic process.

In addition to their unexpected drop topology [13–15]; a model system [17], based on these emulsions, gave a calculated geometry with an unexpected result; an inversion took place in the part of the Janus drop with the lower interfacial tension towards water. The original configuration (O1 + O2)/W was inversed to

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(W + O1)/O2 at a critical partial surface coverage of the O1 drop surface towards water by O2, when the volume of the latter approached infinity. This outcome represents a significant extension of earlier contributions [7,8,12] and, in the present contribution, details of this rearrangement are analyzed for events close to the point of inversion and the features will be related to the general literature on emulsion inversion in Section 4. So far there is no experimental information on such an inversion in Janus emulsions; the example, so far found, is the change from a (VO + SO)/W (VO and SO are vegetable and silicone oils) to a complex (VO + SO)/W/VO/SO emulsion with increased SO volume [15].

2. Fundamental background

The equilibrium topology of Janus drops in an emulsion (O1 + O2)/W depend on two independent factors; the interfacial tension equilibrium at the line of contact between the three liquids and the relative volumes of the two oils. Of these, the first aspect depends only on the compounds per se, while the second element is an independent variable, decided by the preparation process. These factors have been thoroughly examined [7,8,16,17] and the following narrative is condensed, since the thesis of the investigation is restricted to the inversion process per se.

Fig. 1 shows the geometrical details of a Janus drop, with the volumes of the three caps O1 to O3 based on the plane of the contact line between the three liquids, the solid straight line between O1 and O2 in the figure. The volume of O3, $\phi_{O3,}$ in the example consists of the part of O1 protruding into O2 and is introduced solely to facilitate calculation of the volumes. In the example the volume of O1, $V_{O1} = \phi_{O1} + \phi_{O3}$, while $V_{O2} = \phi_{O2} - \phi_{O3}$.

The correlation between the three radii in Fig. 1 and the angles β and δ has been published [14] and is available under Supporting material, while the following section focuses on the specific features of relevance for the inversion. The central feature is the variation of radius $r_{O2/W}$ with the angle μ, (r_2 in the figure). One finds that $r_{O2/W} \to \infty$ for $\mu \to 180°$; i.e. $\eta = 180° - \beta$. This point also represents $V_{O2} \to \infty$ and signifies the limit of the fraction of O1 covered by O2 with increased addition of the latter, with retained configuration (O1 + O2)/W. However, formally calculating $r_{O2/W}$ for $\eta > 180 - \beta$, results in an unanticipated outcome. In this range the radius becomes negative with a trend according to Fig. 2, which presents an example of the radius versus the fraction of O1 covered by O2.

The radius of O2 in the figure goes from +∞ to −∞ at a crucial value of the coverage of the O1 surface by O2, corresponding to a critical value of the angle μ, Fig. 1. At a first glance negative radii

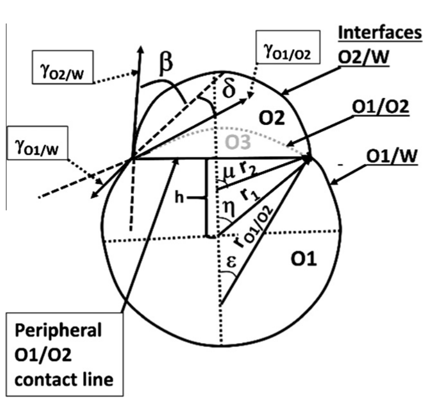

Fig. 1. Interfacial tensions, angles and distances in a Janus drop. The grey dotted line above the grey "O3" shows a projection of the true interface between O1 and O2, while the contact line at the peripheries is given as the straight horizontal line. The radii $r_{O1/W}$ and $r_{O2/W}$ are marked as r_1 and r_2 for space reasons.

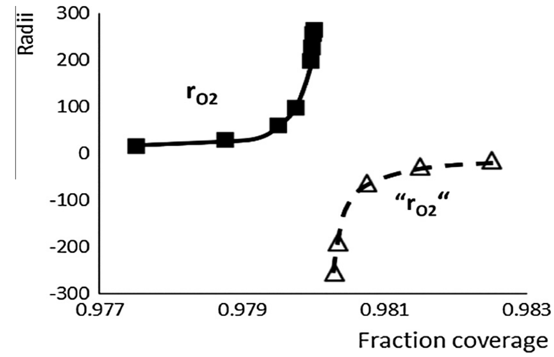

Fig. 2. The radius of O2 versus fraction of O1 covered by O2 for the case of $r_{O1/W}$ equal to unity. The inversion takes place at a coverage of 0.980 corresponding to $\mu = 180°$. The r_{O2} is short for $r_{O2/W}$ and "r_{O2}" is the radius of the drop of the water part in the emulsion (W + O1)/O2, formed after the inversion.

may be perceived as "imaginary", but a rational geometrical arrangement offers a realistic interpretation, as illustrated in Fig. 3.

The figure illustrates the change, when μ transcends 180°. The negative radius for $\mu > 180°$ means that the O2/W curvature has changed sign and the topology now is (O1 + W)/O2 instead of (O1 + O2)/W as indicated in Fig. 2. However, the behavior at $\mu = 180°$ cannot be described in a cartoon like the one in Fig. 3, because the figure reflects conditions in space-limited systems, an approach that gives no guidance, when infinite numbers are involved. Of course, the radius, Fig. 2, changes sign at the inversion point and in the algebra the W volume appears with a negative sign. Hence the volume function cannot be continuous, but a more realistic model would picture the volume as positive and the question is, if the volume function under such circumstances would be continuous.

The question is answered by calculating the absolute value of the radius. The essential equations in the Supporting material section are now written

$$r = |\sin\eta / \sin(\eta + \beta)| \quad (1)$$

or

$$r = |f(x)/f(x + c)| \quad (2)$$

and

$$dr/dx = (f'(x)f(x + c) - f(x)f'(x + c))/(f(x + c))^2 \quad (3)$$

For $\mu = 180°$, $f(x + c) = 0$, while $f(x) \neq 0$ and $f'(x + c) \neq 0$; i.e. $dr/dx \neq 0$ for $x + c$.

In short, the function $|f(x)/f(x + c)|$ is not continuous between angles $\mu - \upsilon$ and $\mu + \upsilon$, in which $\upsilon \to 0$. Hence, the volumes of O2

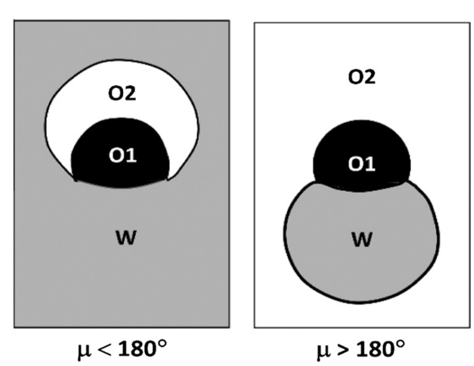

Fig. 3. Illustration of partial Janus emulsion inversion. For $\mu < 180°$ the emulsion is (O1 + O2)/W, while for $\mu > 180°$ the configuration is (W + O1)/O2.