



Feature Article

Emulsion Thermodynamics – In from the Cold

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Abstract. Thermodynamics has played virtually no role in traditional emulsion research, because emulsions are inherently thermodynamically unstable. The problem with commercial emulsions needing to exist with none or only small changes during use and the industrial stability problem was resolved by formulating *colloidally stable* emulsions, i.e. the *rate* of destabilization was reduced. This approach was successful for single-oil emulsions, but encountered problems for double emulsions, for which the simultaneous stabilization of several interfaces within one drop encountered difficulties. Naturally, even for such an emulsion, colloid stability is the only option to stabilize the outer surface towards the continuous phase. In fact, the destabilization by flocculation/coalescence proceeds similarly to a single-oil emulsion. But experiments have demonstrated that complex emulsions with a thermodynamically stabilized inner interface *retain* the individual drop topology during the process. This result opens an avenue to significantly facilitate the formulation of a group of commercially important emulsions, because the cumbersome multiple emulsion stabilization is reduced to the more trivial single-oil emulsion case.

Keywords. Emulsion stability, colloidal stability, interfacial thermodynamics, janus emulsions, emulsion coalescence.

INTRODUCTION

The first meal humans and many animals enjoy is an oral *emulsion* that replaces the nutrients through the umbilical cord. The emulsion in question is a convenient and efficient means to provide the needed mixture of fats, sugars and proteins, which otherwise would be solid and not useful to a toothless newborn. Since these emulsions are truly essential, baby milk emulsions have been commercially available for 150 years for the cases, where the mother does not have milk, or does not want to breast feed. The initial modest introduction by Henry Nestlé has grown to a company with almost \$100 billion in yearly sales, reflecting the commercial expansion to other food emulsions, such as cream, butter and ice cream, to mention the most obvious (Among the miniscule, but common, applications of milk is to remove the bitter taste from coffee - and in some societies from tea - an insult to the refined Oriental cuisine culture). In addition, emulsions also have a long history in personal care and cosmetics with Cleopatra taking baths in donkey milk about 2000 years ago.

This pioneering use of emulsions has developed into a Schueller/Bettencourt company, L'Oreal (actually partly owned by Nestlé), which has grown from a modest start in 1909 to an internationally large company with sales at the level of tens of billions of dollars. These are examples of large applications of emulsions for humans, like emulsions in the paint and coatings industry, which add another huge sum.

All these tremendous volumes of products, which are daily handled all over the world, are, in fact, thermodynamically unstable compositions, doomed to final separation of the components. Nonetheless, the compositions are required to remain virtually unchanged for specific times, varying from seconds to years, depending on the actual purpose. Hence, an extensive volume of research¹⁻³ is found on their properties and especially their "stability". This "stability", is defined as an unchanged appearance reflecting the commercial needs. A more quantitative measure of emulsion stability would be its half-life, e.g. the time for the number of drops to be reduced to one half by coalescence, Figure 1.

As a contrast, the so called microemulsions are not emulsions; they are equilibrium colloidal *solutions*^{4,5} and have been investigated for different aspects of their interfacial properties.⁶⁻⁸ Because they are thermodynamically stable, their preparation is completely different from that of emulsions. These latter are prepared, in most cases, by mechanically dividing a liquid into drops and dispersing these in a continuous liquid, while microemulsions are spontaneously formed,⁵ requiring only the most minute mixing for large volumes. The microemulsions are of considerable commercial interest, (reflected in about half a million Google hits) but are not the subject of the present contribution, which is focused on emulsions.

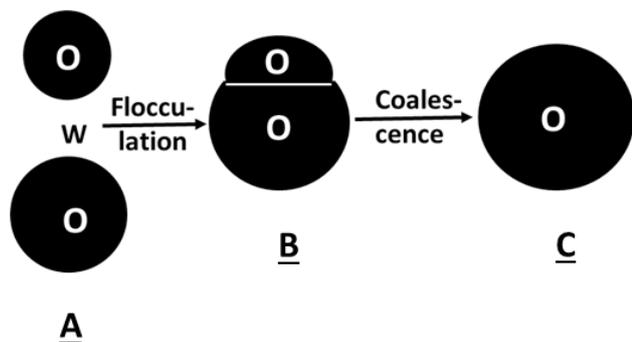


Figure 1. Two emulsion drops of one oil, A, are colloiddally stabilized and, when they aggregate (Flocculation, A to B), they form an aggregated drop of transitory stability, B. The transient interface dividing them (white line, B) is destabilized and coalescence (B to C) occurs to a single drop, C.

Their comprehensive and advanced treatments¹⁻³, in turn, examine emulsion stabilization from the viewpoint of *colloidal stability*, applying the concepts from the DLVO theory,⁹⁻¹¹ in which a *repulsive force* is introduced between drops to reduce *the rate* of flocculation and coalescence. This action naturally does not make the emulsions thermodynamically stable, but tender serviceable information to retain the properties of traditional emulsions for commercial purposes. This colloidal stability approach was also employed for double emulsions,¹² whose more complex topology caused challenging stability problems.^{13,14}

In summary, except for in the area of microemulsions, there was no significant need, nor even a role, for thermodynamics in emulsion research; a mindset that has recently experienced an initial conversion, when Janus emulsions were introduced.^{15,16} These emulsions consist of combined drops of two mutually insoluble oils, Figure 2, in which total free interfacial energy of the single drop is significantly less than that of the oils in separate drops. Hence, their "inner" topology, Figure 2, is thermodynamically stabilized,¹⁷⁻¹⁹ and actually has been shown to survive most of the flocculation/coalescence process.²⁰

A brief comment at this stage is necessary to avoid misinterpretation. Janus emulsions are *not* thermodynamically stable, like microemulsions. The Janus emulsions, as a contrast, undergo a flocculation/coalescence process and, *if left for sufficiently long time, will separate into three, or four liquid layers, depending on the relative density*, because of gravitational forces. Nevertheless, the feature mentioned in the last part of the former paragraph is significant, because it brings to light a new approach to formulating emulsions with two-oil drops.

Traditionally, commercial double emulsions are prepared either by first forming an oil/oil emulsion followed

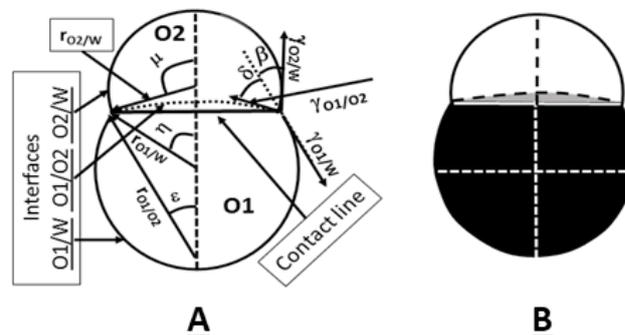


Figure 2. A. The geometry and interfacial tensions in a Janus drop. B. Black, O1 volume limited by the contact line, White, O2 volume limited by the contact line, Grey, O1 volume penetrating the O2 space from the contact line.

by its emulsification in an aqueous phase (O1/O2)/W or by emulsifying one oil in water, followed by emulsification of this emulsion into the second oil plus a final emulsification into an aqueous phase (O1/W/O2/W). All the preparations necessitate *independently* stabilizing the different interfaces by colloid stabilization; a methodology, beset with a main problem. The transfer of surfactant stabilizers between the liquid phases, which would markedly reduce their stabilizing action, was successfully overcome for individual emulsions after a substantial amount of outstanding research.^{13,14} Conversely, in the alternative methodology using thermodynamic stabilization, the stabilizer is allowed freely to equilibrate between phases, as long as *the level of surface tensions are in the order* defined in later sections. With this approach, colloidal stabilization is limited to the outer interface towards the aqueous phase, a simpler problem, which has been extensively treated.¹⁻³

In summary, the focus of the attention is shifted from colloidal stabilization, a kinetic phenomenon, to interfacial tensions, a quantifiable equilibrium entity. The transition from one preparation method to the other requires a change in the mind set and the present contribution is an attempt partially to outline the relevant thermodynamic framework.

THERMODYNAMIC STABILIZATION AND INTERFACIAL TENSIONS

The basis for the thermodynamic framework is the equilibrium of three tensions in one plane, Figure 3. These tensions act at the contact line, Figure 2, and, combined with the relative volume of the two oil lobes, determine the equilibrium topology of the combination drops. As a result, they are central to this contribution and a summary of their ramifications is useful for the continued analysis with appropriate limitation. The features of Figure 3 are relevant only for a case in which $\gamma_{O1/W} < \gamma_{O2/W} + \gamma_{O2/O1}$ and $\gamma_{O1/W} > \gamma_{O2/W}$ and $\gamma_{O1/W} > \gamma_{O2/O1}$.

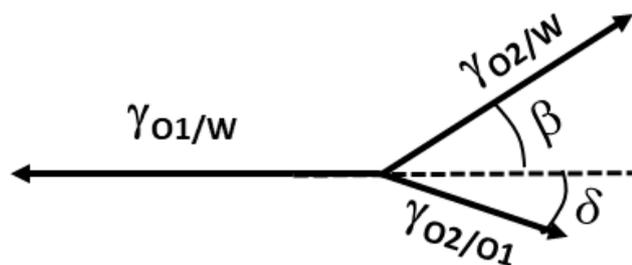


Figure 3. Angles β and δ for three equilibrium tensions in one plane.

An analysis of the consequences from inequalities, outside the ones mentioned, is of algebraic interest, but offer no contribution of value to the problem at hand.

Instead, the main theme of this examination is to survey the thermodynamic effect on the topology of Janus and double emulsion drops and it is convenient to divide the range of tensions into two parts. The first part of the range covers $\gamma_{O1/W} > \gamma_{O2/W} + \gamma_{O2/O1}$ (relevant for double emulsion drops), followed by $\gamma_{O1/W} < \gamma_{O2/W} + \gamma_{O2/O1}$, defining the equilibrium in a Janus drop, Figure 2. In addition, the intermediate case of $\gamma_{O1/W} = \gamma_{O2/W} + \gamma_{O2/O1}$ has some features of interest, which will be briefly mentioned. The stipulation $\gamma_{O1/W} > \gamma_{O2/W} + \gamma_{O2/O1}$ portends a non-equilibrium *spreading* of O2 or O1 on W, while $\gamma_{O1/W} < \gamma_{O2/W} + \gamma_{O2/O1}$ means a stable *equilibrium* with defined angles β and δ , Figure 2 and 3. For these, one has, with the ratios $\gamma_{O2/W}/\gamma_{O1/W} = a$ and $\gamma_{O2/O1}/\gamma_{O1/W} = b$, equations [1] and [2].

$$\beta = \text{acos}((1 + a^2 - b^2)/2a) \quad [1]$$

$$\delta = \text{acos}((1 - a^2 + b^2)/2b) \quad [2]$$

It should be observed that these equations are applicable only to the equilibria in Figure 3, and may be used to calculate the interfacial free energy as such for a selected drop topology, but the calculations fail to identify the thermodynamically *preferred* topology. This topology is obtained first, when the free energy quantity is contrasted with that of a counterpart. The free energy number per se actually implies a counterpart with *no interfacial free energy* and the approach would show *any* selected topology to be thermodynamically disfavored and is of no use to judge thermodynamic stability. In addition, the free energy of two-oil emulsion drops also depends on the volume ratios of the two oils and an equitable, but injudicious, choice of a reference topology will result in erroneous conclusions. This fact will later be brought to light.

Equations [1] and [2] relate the angles β and δ to tensions at equilibrium, but not in an explicitly illustrative manner and a few numbers from a model system are informative as a graphic. Figure 4 shows the limitations of the angles β and δ versus the $\gamma_{O2/O1}/\gamma_{O1/W}$ (b) with $\gamma_{O2/W}/\gamma_{O1/W}$ (a) as parameter. The range of the two variables in the figure is limited in order to reflect the conditions in Figure 3. So, are numbers for $b > 1$ excluded, because they would represent a reorganization of the angles in the figure. The δ limit for $a=1$ varies as $\delta = 60 + 30(1 - b)$ (degrees) for the same reason.

The numbers for the δ angle shows the development of the equilibrium/spreading border, Figure 4 C,

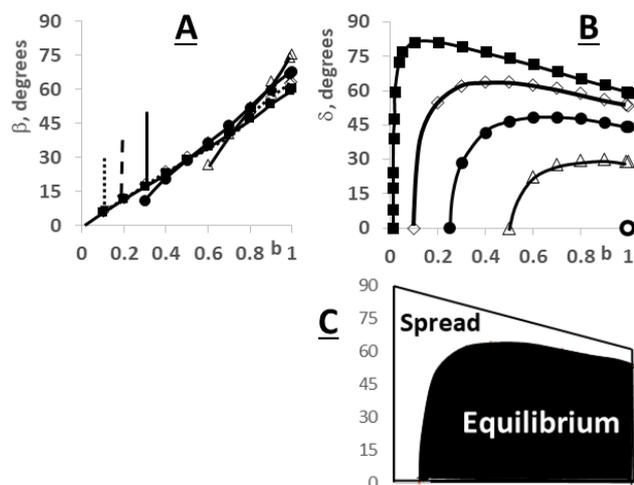


Figure 4. Angles β (A) and δ (B) and areas of equilibrium and spreading (C) versus the ratio $\gamma_{O_2/O_1}/\gamma_{O_1/W}$ (b). The ratio $\gamma_{O_2/W}/\gamma_{O_1/W}$ (a) is the parameter with the following numbers. ■, 0.99; ◇, 0.90; ●, 0.75; △, 0.5. The minimum b number for each a is marked with an arrow; ◇, 0.90, dotted; ●, 0.75, dashed; △, 0.5, full line. For ○, $\gamma_{O_1/W}$ implicitly equals unity.

with varied $\gamma_{O_2/W}/\gamma_{O_1/W}$ (a). The artificial δ value for $a = 0$ (The oils are mutually completely soluble) is a single point with $\delta = 0$, because, since $\gamma_{O_2/W} = 0$ and $\gamma_{O_2/O_1} = \gamma_{O_1/W}$, the number for angle b becomes irrelevant. In fact, the entire area (except $b = 1$) denotes spreading. Increasing the $\gamma_{O_2/W}/\gamma_{O_1/W}$ (a) values from zero, results in an expansion of the equilibrium part of the area, reaching the entire area for $a = 1$. Any number for $a < 1$, however close, e.g. $1 - \epsilon$ (epsilon small) means a 2ϵ wide area of spreading along the $b = 0$ axis and ϵ broad along the axis for maximum δ .

After this brief review of the ramifications for the conditions in Figure 3, the following sections analyze the interfacial free energy of a single *drop*, omitting the emulsion inter-drop dynamics. The analysis of the double emulsion drop is built on the inequality $\gamma_{O_1/W} > \gamma_{O_2/W} + \gamma_{O_2/O_1}$, and the spreading means that the O2/W interface does not exist. The drop instead consists of a larger drop O1/W with an O2/O1 drop inside, in accordance with the thermodynamic condition. Conversely, the O/W interface is thermodynamically unstable for virtually all positive $\gamma_{O_1/W}$ and an assembly of such drops will coalesce like the simpler single-oil emulsions.

Hence, the potential thermodynamic stabilization is limited to the *inner* interface of the drop, while the initial coalescence is exclusively concerned with its colloidal stabilized outer surface, as has been shown for Janus emulsions.²⁰ Hence, at a first glance, the thermodynamic stabilization of the inner interface may be considered only of minor importance, but the extensive

research on double emulsions¹²⁻¹⁴ indicates otherwise. In fact, with the “inner” interface of Janus or double emulsion drops thermodynamically stabilized, the only stabilization needed for a commercial double emulsion would be for the interface towards the continuous phase; i.e. a problem, that has been solved using the colloidal stability approach.¹⁻³ The only requirement for the O1/W stabilizers is that the interfacial tensions obey the stated inequality; a non-specific condition.

Hence, considering the future potential for a new line of formulations and the fact that virtually no information exists, a review of the thermodynamics of both a double emulsion and a Janus drop has merits. The examination is initiated at a double emulsion drop, because of the extensive technical and commercial relevance for such emulsions.¹²⁻¹⁴

DOUBLE EMULSION DROP

Double emulsions have wide use within a number of industries and technologies, as described in a recent and comprehensive review.¹² The extensive and high-quality research within the area^{13,14} has applied the colloidal stability approach, illustrating the enhanced difficulties, compared to those of simple emulsions. The problem arises, because of the fact that two interfaces have to be *independently* stabilized.^{13,14} A surfactant, acting effectively on the O/W interface, has to be prevented from diffusing towards the O/O interface and vice versa, reducing its stabilizing action.

However, the results of recent studies of the destabilization of Janus emulsions²⁰ have demonstrated a substantial effect of interfacial thermodynamic factors to modify the coalescence process of these emulsions. In fact, the Janus topology was retained during coalescence until the very last stages.²⁰ No such experimental results have been reported for double emulsions, but the potential for such an outcome is estimated sufficiently positive to justify a section on their interfacial thermodynamics in the present publication. Hence, the interfacial thermodynamics of a double emulsion drop is examined to outline its prospective stabilizing effect, with a view towards the effect found for Janus emulsions.

The interfacial free energy basis for a double emulsion drop is the inequality $\gamma_{O_1/W} > \gamma_{O_2/W} + \gamma_{O_2/O_1}$, which, as mentioned, shows non-equilibrium *spreading* with an appealing application of this condition to estimate the thermodynamic stability of a double emulsion drop. However, this kind of interpretation has to be made with caution, because the term thermodynamic stability is defined only against a specific counterpart. A seemingly

attractive such system is two separate drops of the single oils, but leads to thermodynamic contradictions, showing this stabilization outside the mentioned inequality. Nonetheless, such a choice per se has distinct algebraic interest, combining a well delineated interfacial free energy and an easily comprehended connection to the destabilization of physical emulsions. The following evaluation focuses on the overall free energy difference between a double emulsion drop and two single-oil drops. The volume *fraction* of oil 2 in the drop is v_{O2} and the interfacial free energy of the drops are offered in Table 1.

Table 1. Interfacial free energy of double emulsion drops.

Configuration, drops	IFE, O1	IFE, O2
Double drop	$4\pi(0.75/\pi)^{(2/3)}\gamma_{O1/W}$	$4\pi(0.75v_{O2}/\pi)^{(2/3)}\gamma_{O2/O1}$
Separate drops	$4\pi(0.75(1-v_{O2})/\pi)^{(2/3)}\gamma_{O1/W}$	$4\pi(0.75v_{O2}/\pi)^{(2/3)}\gamma_{O2/W}$

Regrettably, there is no direct algebraic expression for the relationship between free energy and volumes for the calculation.^{18,21} Instead a realistic example was selected to illustrate the variation in free energy during a coalescence process. The particular emulsion consists of $1.09 \cdot 10^9$ internally thermodynamically stabilized double emulsion drops, each with a volume of $4.188 \cdot 10^{-15} \text{ m}^3$. The two oils O1 and O2, with interfacial tensions 0.004 N/m ($\gamma_{O1/W}$), 0.00262 N/m ($\gamma_{O2/W}$) and 0.00116 ($\gamma_{O1/O2}$) each occupy one half. The drops are coalesced, two and two, 30 times, leaving only one final drop with a volume of $4.05 \cdot 10^{-6} \text{ m}^3$ and retained topology. The coalescence covers the free energy change due to interface size increase of both the outer sphere and the inner one, of which the former contributes a majority of the free energy reduc-

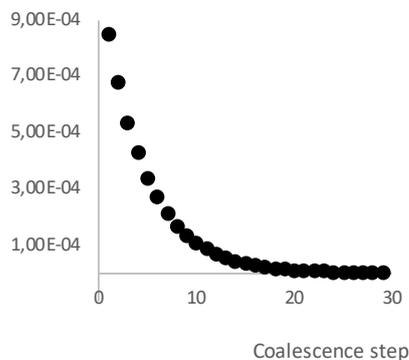


Figure 5. The difference in interfacial free energy (See text).

tion. As is obvious and expected, the emulsion interfacial free energy is exponentially reduced, Figure 5, during coalescence; a reflection of the thermodynamic overall instability of emulsions; even when the drops contain more than one interface.

The overall reduction in interfacial free energy is certainly expected, but a more essential issue is a comparison of the free energy change, when two double emulsion drops coalesce into one double emulsion drop or to two single oil drops, O1 and O2, during the coalescence. Figure 6 depicts this difference between interfacial free energy change from two Janus drops, when a double emulsion drop, ●, or two separate drops, △, form.

The results in Figures 5 and 6 are unequivocal; the coalescence to a single double emulsion drop implies an expected *reduction* of free energy, while the alternative means an *increase*. These results are remarkable and conclusions would unquestionably be tempting; both about the general validity of the result and vis-à-vis the technical and commercial effects. Nevertheless, such inferences would be premature at this stage, because a more complex geometry after coalescence will, in some cases, lead to a modified result. Even so, the results encourage future experimental and numerical evaluations. Leaving that aspect temporarily aside, even the more fundamental aspects offer some unexpected results, illustrated by the ratio, $R_{C/D}$ between the interfacial free energy of the combination drop and that of the two separate drops, equations [3] and [4]. v_{O2} is fraction of O2 volume.

$$R_{C/D} = \text{IFE}_{\text{comb dr}} / \text{IFE}_{\text{sep dr}} \quad [3]$$

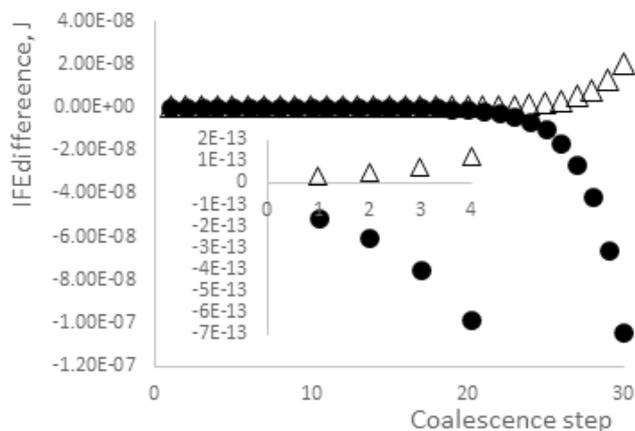


Figure 6. The free energy changes, when two double emulsion drops (Example in text) coalesce to form one double emulsion drop, ●, or two single oil drops, △, of O1 and O2, respectively.

$$R_{C/D} = \frac{[(1 - v_{O2})^{2/3}\gamma_{O1/O2} + \gamma_{O2/W}]}{[(1 - V_{O2})^{2/3}\gamma_{O1/W} + v_{O2}^{2/3}\gamma_{O2/W}]} \quad [4]$$

According to these conditions, there are examples, Figure 7, which indicate ranges outside the condition $\gamma_{O1/W} > \gamma_{O2/W} + \gamma_{O2/O1}$, at which the combined drop is thermodynamically favorable to two separate drops.

The interfacial free energy of the double emulsion drop is unquestionably less than that of the two separate drops for *all* volume ratios, when $\gamma_{O1/W} > \gamma_{O2/W} + \gamma_{O2/O1}$. Then again, for $\gamma_{O1/W}/(\gamma_{O2/W} + \gamma_{O2/O1}) = 0.85$ (curve \diamond in Figure 7) the ratio in question is still less than one; an obvious thermodynamic contradiction. If there is no spreading, it is difficult to accept that two separate drops should spontaneously unite to a double emulsion drop. Nonetheless, neglecting the fundamentals, focusing on the algebra per se, the trend as such of the curves in Figure 7 is anticipated from equations [3] and [4]. The initial increase of the first term of the equation denominator is less than that of the numerator of the equation, giving a downward slope, while the final change is the opposite, giving the minimum of the curve. As a result of the shape of the curves, the $R_{C/D} < 1$ within a limited range of relative volumes, even for $\gamma_{O1/W} < \gamma_{O2/W} + \gamma_{O2/O1}$, a purely algebraic result. However, the indisputable conclusion is that the use of two separate spheres is not the

correct counterpart to gauge the thermodynamic stability of a double emulsion drop. In fact, the choice of a correct counterpart to evaluate the thermodynamic stability of the double emulsion drop needs a more comprehensive evaluation of the entire tension range.

Another small detail in Figure 7 might be mentioned, for which the inequality $\gamma_{O1/W} > \gamma_{O2/W} + \gamma_{O2/O1}$ actually is directly applicable to a physical emulsion. The final outcome of the coalescence of a double emulsion, whose interfacial tensions obey the inequality in question, is in the form of three layers of the liquids. At that point, gravity decides the order of the layers in the container. If the liquid densities vary as $\rho_W > \rho_{O2/W} > \rho_{O1/W}$, the order of the three layers will be O1, O2 and W from the top and three layers are found. Conversely, if the densities are ranged $\rho_W > \rho_{O1/W} > \rho_{O2/W}$, four layers are found, since the O1 layer is not in direct contact with the water layer, but separated from it by an (infinitely thin) O2 layer, because O2 spreads on W. Needless to say, these results are based on single-oil drops as the alternative to the double emulsion drop. In reality, a double emulsion drop will not change to two individual drops, if interfacial tension ratio is moved outside the condition $\gamma_{O1/W} > \gamma_{O2/W} + \gamma_{O2/O1}$. This will become evident in the analysis of *the entire range* of interfacial tensions, which shows that, for $\gamma_{O1/W} < \gamma_{O2/W} + \gamma_{O2/O1}$, the preferred topology becomes that of a Janus drop.

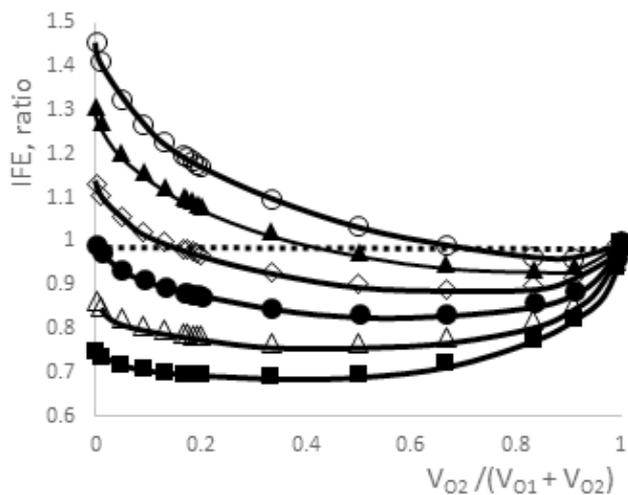


Figure 7. The IFE ratios between the interfacial free energy of a double emulsion drop and two separate single-oil drops with $\gamma_{O1/W} = 1$.

Symbol	$\gamma_{O2/W}$	$\gamma_{O2/O1}$
■	0.5	0.25
△	0.58	0.29
●	2/3	1/3
◇	0.78	0.39
▲	0.88	0.44
○	0.98	0.49

JANUS DROP

The introductory publication on Janus emulsions¹⁵ was based on microfluidics¹⁶ emulsification. This preparation guarantees emulsions at virtual internal equilibrium and led to a number of investigations into the different aspects of Janus drops,¹⁷⁻²² the results of which confirmed the agreement between equilibrium predictions and experimental results. These studies formed the basis for an extensive foray into several important aspects of emulsions in biology and medicine, led by Weitz.²³ The method, as such, enabled the preparation of emulsions, to all intents and purposes, of *any* complex topology, but was inherently limited to diminutive volumes, preventing applications into commodities. This condition was changed in 2011, when Hasinovic et al prepared Janus emulsions by traditional vibrational emulsification,²⁴ opening an avenue to large scale production. This pioneering contribution showed microscopy photos of well-defined Janus emulsions, Figure 8.

The image shows well defined drops of an O/W Janus emulsion of a vegetable oil, weight fraction 0.18

and a light silicone oil, weight fraction 0.72, while the continuous aqueous phase comprises only 0.1. It is noteworthy that an O/W emulsion with such limited volume of continuous phase is formed in a standard vibrational emulsification; an early indication of the unexpected effect of interfacial thermodynamics on vibrational emulsification process. Furthermore, but equally important, the regular Janus topology was first achieved by shear *after* the initial emulsification. Both processes were necessary in most cases and deserve separate comments.

The emulsification as such is a process, in which a large number of transitory small drops of irregular shape are formed and the freshly prepared emulsion is a result of these drops rapidly coalescing to larger entities.²⁵ This process will favor irregular Janus drops for kinetic reasons, because there is virtually no colloidal stability effect involved. Assume an equal number, n , of equally sized drops of two mutually insoluble oils, which are allowed to coalesce at a rate, which is independent of specific drop topology. Subsequent coalescence of these drops leads to an overwhelming fraction of irregular shape Janus drops, in addition to their larger sizes. During the ensuing shear the small attached O2 drops coalesce to a regular Janus lobe. The effect of shear was cursory illustrated^{26,27} by optical microscopic images, before and after a cover glass was applied on the microscope slide, Figure 9. The minute shear from the cover glass resulted in fewer drops, as expected, but also in an extensive topology change to better defined Janus drops.

In addition, the results of shear also – albeit indirectly – serve to confirm the internal thermodynamic stability of the Janus drops. Contrary to the case for single-oil emulsions, for which the effect of shear *at low rates* is to form larger spherical drops, low rate shear of

the initial Janus drops, left micro-photo Figure 9, leads to coalescence of the attached drops and a more regular Janus drop. As such, the information in Figure 9 also complements and supports later experimental proofs of the thermodynamic stability of the structure.²⁰

These results are concerned with the kinetic factors of the process, leaving the thermodynamics unexamined. The equilibrium angles and tensions of the Janus drop are given in Figure 2A and the algebra for equilibrium has been reported^{16-19,27,28} with the following summary.

Balancing the forces in Figure 2A along and perpendicularly to the $\gamma_{O1/W}$ direction gives the angles β and δ , Figure 2A, which, in turn, define the angles μ and ϵ .

$$\mu = \eta + \beta \quad [5]$$

$$\epsilon = \eta - \delta \quad [6]$$

Furthermore, assuming $r_{O1/W} = 1$, the radii $r_{O2/W}$ and $r_{O2/O1}$ are

$$r_{O2/W} = \sin\eta/\sin\mu \quad [7]$$

$$r_{O2/O1} = \sin\eta/\sin\epsilon \quad [8]$$

These equations control the equilibrium at the contact line, while the entire drop configuration, Figure 2B, also depends on the relative volumes of the two dispersed liquids. Unfortunately, the latter feature is not easily calculated from given volume fractions. The expressions become prohibitively complex and Guzowski et al¹⁸ opted to use a computer program to correlate volumes and topology. As an alternative, the volumes are calculated in the present contribution from the geometrical features in Figure 2 and the correlations between

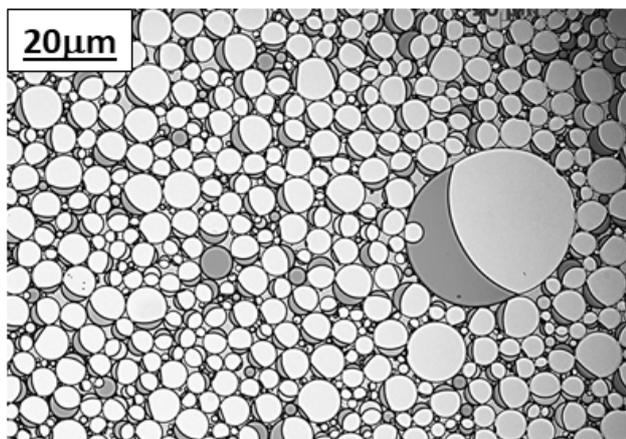


Figure 8. An optical microscopy image of a Janus emulsion, prepared by vibrational emulsification.

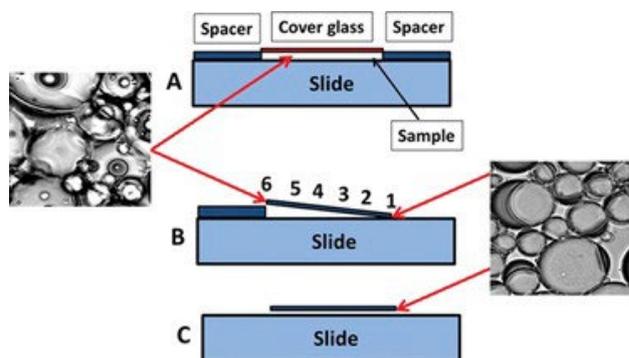


Figure 9. A simple experiment illustrating the effect by shearing on a Janus emulsion, prepared by vibrational emulsification²⁷. (From reference 27 with permission).

volume ratios and topology are evaluated ex post facto.^{26,28}

The volumes of O1 and O2 are calculated (equations [12] and [13]) via pre-volumes, φ_{O1} , black, Figure 2B, and φ_{O2} white + grey, Figure 2B, separated by the plane through the visible contact line.

$$\varphi_{O1} = \pi(1 + \cos\eta)^2(2 + \cos\eta)/3 \quad [9]$$

$$\varphi_{O2} = \pi(r_{O2/W} - \cos\mu)^2(3 - r_{O2/W} + \cos\mu)/3 \quad [10]$$

The volumes V_{O1} and V_{O2} are attained from φ_{O1} , φ_{O2} and $\varphi_{O1/O2}$ (Grey, Figure 2B),

$$\varphi_{O2/O1} = \pi r_{O2/O1}^3(1 - \cos\epsilon)^2(2 + \cos\epsilon)/3 \quad [11]$$

$$V_{O1} = \varphi_{O1} + \varphi_{O2/O1} \quad [12]$$

and

$$V_{O2} = \varphi_{O1} - \varphi_{O2/O1} \quad [13]$$

In the comparison of interfacial free energies, the single-oil drops as counterparts are now replaced by a direct comparison between the free energies of double emulsion and Janus drops. As will be demonstrated, this new comparison is more relevant, removing the ‘‘anomalous’’ results in Figure 7. This figure showed the double emulsion drop to have lower interfacial free energy than two separate single-oil drops in a limited range of volume fractions, even for $\gamma_{O1/W} < \gamma_{O2/W} + \gamma_{O2/O1}$. The reason for this result is that the free interfacial free energy of the Janus drop was neglected, as has commonly been the case. Figure 10 shows the ratio of the free interfacial

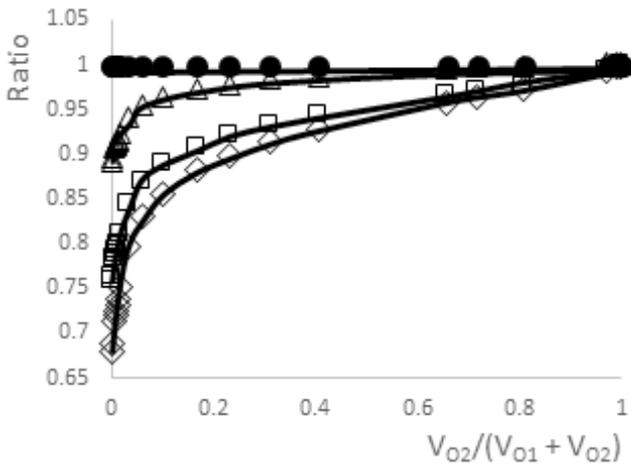


Figure 10. The ratio of Interfacial free energy of a Janus drop and a double emulsion drop of identical oil volumes.

energies of a Janus drop to those of a double emulsion drop of identical volume. The ratio was limited to the tensions $\gamma_{O1/W} < \gamma_{O2/W} + \gamma_{O2/O1}$; since the drop equilibrium free energies for Janus drops with $\gamma_{O1/W} > \gamma_{O2/W} + \gamma_{O2/O1}$ is outside the equilibrium conditions and cannot be exactly calculated.

The figure demonstrates the Janus drop to have a lower free energy than the double emulsion drop in the inequality range $\gamma_{O1/W} < \gamma_{O2/W} + \gamma_{O2/O1}$. The faulty conclusion from using two single-oil drops as counterpart is now corrected.

In addition, there are two details that are of interest. The topology change, when the inequalities change from $\gamma_{O1/W} < \gamma_{O2/W} + \gamma_{O2/O1}$ to $\gamma_{O1/W} > \gamma_{O2/W} + \gamma_{O2/O1}$ is of special interest, because it is highly prominent. A complete analysis involves a large number of variables and in the present contribution a simplified example is used to graphically illustrate the phenomenon. The basis for the example is the specific and well defined case $\gamma_{O1/W} = \gamma_{O2/W} + \gamma_{O2/O1}$. In the calculation the expression is divided by $\gamma_{O1/W}$, giving $\gamma_{O2/W} = a$ and $\gamma_{O2/O1} = 1 - a$. The change of inequalities mentioned is represented by $\gamma_{O1/W}$ altered from $1 - \epsilon$ to $1 + \epsilon$, in which ϵ is a small positive quantity. The angles b and d are calculated with the $\gamma_{O2/W}$ and $\gamma_{O2/O1}$ equal as are the O2 and O1 volumes. The specific selection of these is not essential for the central theme, and the angles β and δ are calculated versus ϵ .

$$\cos\beta = \cos\delta = 1 - (2 - \epsilon)\epsilon \quad [14]$$

The radical topology change, caused by the minute alteration of $\gamma_{O1/W}$ from 0.995 to 1.005 is illustrated in Figure 11.

The minute increase (1%) of the interfacial tension $\gamma_{O1/W}$ causes a drastic topology change with O1 spreading on the large sphere of O2. The activity is the same for smaller ϵ , but the graphics becomes less instructive, because the visible contact line is transferred to greater η angles with reduced ϵ .

Another, perhaps even more drastic consequence, is found of the interfacial tension variation for model sys-

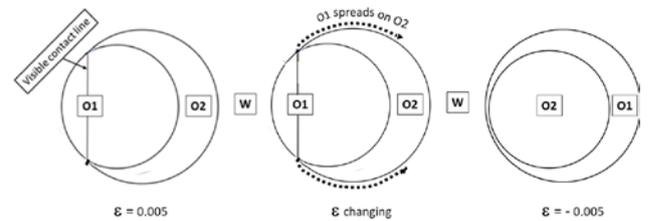


Figure 11. With $\epsilon = 0.005$, $\gamma_{O1/W} < \gamma_{O2/W} + \gamma_{O2/O1}$, a Janus drop is thermodynamically preferred. When ϵ changes to -0.005 , O1 spreads on O2 and a double emulsion drop is favored.

tems with realistic interfacial tensions.²⁸ As an example, the variation of $r_{O2/W}$ and $r_{O2/O1}$ ($r_{O1/W}=1$) with η is truly remarkable, Figure 12, for $\beta = 27.8^\circ$, $\delta = 35.4^\circ$, $\gamma_{O1/W}=1$ and $r_{O1/W} = 1$. Each curve has a discontinuity, at which an infinite radius switches to the opposite sign with changing η . The $r_{O2/O1}$ versus η switches from $-\infty$ to $+\infty$ at $\eta = \delta = 35.4^\circ$, while r_{O2} versus η discloses a discontinuity at $\eta = \pi - \beta$, approximately $\eta = 152.4^\circ$, Figure 12.

The discontinuity of $r_{O2/O1}$ at $\eta = 35.4^\circ$, has only a small effect on the volumes of the two lobes, Figure 2. Instead, the influence is felt on the Laplace pressure correlation.

$$\Sigma 2\Delta P_{XX}/r_{XX} = 0 \quad [15]$$

The radius $r_{O2/O1}$ is negative for $\eta < 35.4^\circ$, Figure 2. In this η range the terms $\gamma_{O2/W}/r_{O1/W} < 1$ and hence necessitates a negative $r_{O2/O1}$ to satisfy the LaPlace requirements, equation [15]. For $\eta = 35.4^\circ$, the $\gamma_{O2/W}$ and $r_{O2/W}$ both are 0.65 and, again the Laplace pressure condition complies with those in equation [15]. For $\eta > 35.4^\circ$, the sign of the radius is opposite to that at $\eta < 35.4^\circ$. Nonetheless, as mentioned, the effect is not decisive for the size of the volumes, since $\varphi_{O2/O1}$ is usually small compared to volumes φ_{O1} and φ_{O2} , equations [9] and [10].

Conversely, the change in r_{O2} is accompanied by an extreme change in the O2 volume. As shown by Friberg²⁸ as well as by Ge et al²⁶ in different examples, at $\eta \approx 154.2^\circ$ for the Janus drop in question, the change represents a partial inversion of the Janus drop from (O1 + O2)/W, $\eta = 140^\circ$, Figure 13, to (O1 + W)/O2 $\eta = 164^\circ$.

At $\eta = 140^\circ$, the $r_{O2/W}$ has reached a value of 3.0 with $r_{O1/W} = 1$ and $r_{O2/O1} = 0.66$. The O1 drop is formed by

two lobes, one reaching 0.23 (fraction of $r_{O1/W}$) into W, O1/W, and a second lobe entering 0.83 fraction into O2, O2/O1. There is, needless to say, no interface between the lobes. Together they form a *non-spherical* drop, O1, with an abrupt sign change of the radius as well as its dimension at the contact line. As expected, the added Laplace pressure over the interfaces O2/O1 and O2/W equals the pressure over the O1/W interface.

When η is increased to 152.4° , the O1 drop is located at the interface between two infinite phases W and O2. Nor in this case is the O1 drop symmetrical, since the $\gamma_{O1/W}$ is different from $\gamma_{O2/O1}$ and the LaPlace pressure is equal across the two interfaces of O1. Increasing γ to 164° , Figure 13, shows an (O1 + W)/O2 Janus emulsion and a further reduction of the O1 drop size.

These results and those in the preceding paragraphs are correct illustrations of the drop topology, as directed by the thermodynamic requirements. However, the applications to a physical emulsion are fraught with uncertainties and a few comments on the prerequisites for the model system are useful. The $\gamma_{O1/W} = 1$ is not a cause of concern; it only implies that instead of numerical values for $\gamma_{O2/W}$ and $\gamma_{O2/O1}$, their ratios $\gamma_{O2/W}/\gamma_{O1/W}$ and $\gamma_{O2/O1}/\gamma_{O1/W}$ are used to simplify the algebra. Conversely, the second condition $r_{O1/W} = 1$ causes artificial restrictions on the physical image. It indicates that for each η change, a slice of O1 between the η :s in question is removed and a modified section of O2 is added at the contact line with exactly correct b angle. As is obvious, the conditions, in spite of being thermodynamically correct, are difficult to reconcile with any physical system, especially to the close packing of drops. The second alternative, retaining the O1 volume constant, gives a result similar to the one for constant $r_{O1/W}$, while the more artificial choice of keeping the entire drop vol-

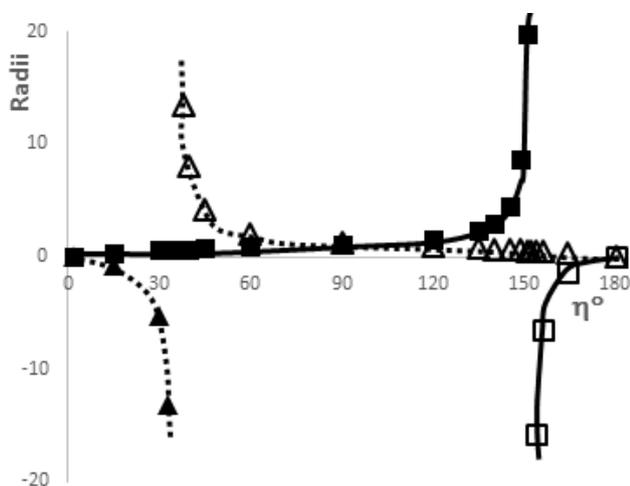


Figure 12. Radii of lobes for the Janus drop, dashed line in Figure 2, with r_{O1} equal to unity. Squares $r_{O2/W}$ triangles $r_{O2/O1}$

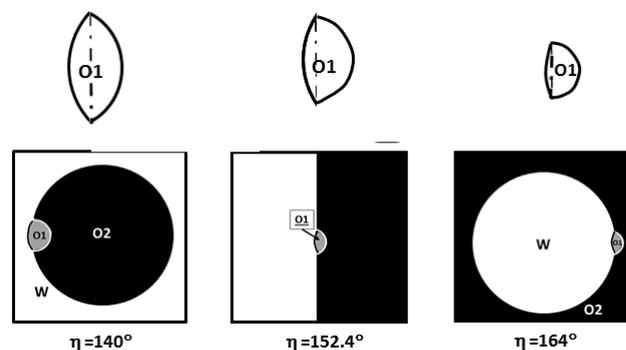


Figure 13. Schematic representation of the inversion of the Janus drop in the range $\eta = 140^\circ - 164^\circ$. Black areas are O2, grey areas O1 and white W. Expanded O1 areas with correct radii ratios are shown on top with the extension of the contact line as dotted/dashed.

ume constant leads to some modification. Nevertheless, from a physical point of view, the second alternative is the most realistic with O2 added to an already formed O1/W emulsion. For this case, adding O2 brings about a greater and greater O2 lobe of the drop, but causes no emulsion inversion, until the volume of O2 is greater than that of the initial continuous phase O1.

As a summary, adding the oils to an initial aqueous liquid gives an O1/W emulsion. Adding O2 to this emulsion results in a Janus emulsion, (O1+ O2)/W, an emulsion with increasingly larger O2 lobes. When the O2 volume exceeds that of the W, an inversion takes place to an (O1 + W)/O2 emulsion. Continued addition of O2 gives rise to a diminution of the relative size of the (O1 + W) drop.

CONCLUSIONS

The conclusions to include Janus emulsions as a counterpart, when considering the thermodynamic factors for double emulsion drops have been proven correct for selected examples.

The extension of these conclusions to Janus and double emulsion drops in general would be premature, but, so far, the indications are that the inference has more general validity.

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